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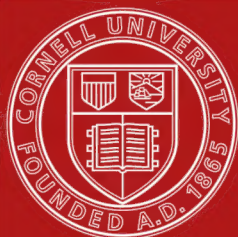
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## **METALLURGY OF COPPER**

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BOOKS BY

**H. O. HOFMAN**

PROFESSOR OF METALLURGY, MASSACHUSETTS  
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BY

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INSTITUTE OF TECHNOLOGY

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1914

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TO  
THE  
*Memory*  
of my  
*Teacher*

DR. WILHELM HAMPE,  
LATE PROFESSOR OF CHEMISTRY AT THE  
ROYAL PRUSSIAN MINING ACADEMY  
OF CLAUSTHAL.

---

ESTEEMED BY METALLURGISTS FOR HIS  
CLASSICAL RESEARCHES UPON COPPER





## PREFACE

My aim in preparing this book has been to furnish a treatise on copper which will meet the demands of the metallurgist of to-day. In order to do this, it has been necessary: to present the leading physical and chemical facts about the metal, its alloys, and its compounds which are of metallurgical importance; to record from the older practice that which is of lasting value; and to give the details of the present modes of operating. Though we have several books treating of certain branches of the metallurgy of copper, such as the valuable volumes of Peters, Greenawalt, and others, there does not exist a modern book which covers the entire ground as the present work aims to do.

In the study of processes there are given the principles and the practice. The discussion of principles is confined to the essential points; for an extended presentation the reader is referred to my treatise on General Metallurgy. The examples of practice are drawn mainly from the United States. The text and footnotes will show that the technical literature on copper has been covered. The details of practice, not recorded in print, have been obtained through visits to and detailed studies of the leading copper smelteries and refineries of the United States; additional information has been available through correspondence. The tables giving the working data of the leading plants of the United States, Canada, Mexico, Germany, and Australia show the extent of the field which has been covered.

In all my visits and correspondence I have met with the greatest cordiality and liberality. I wish to express here my obligation to the heads and officers of the different smelteries and refineries for the assistance they have rendered me in my task; without this cordial and liberal aid it would not have been possible to prepare this treatise.

In working out the details, especially in the large number of calculations, I have been much assisted by the collaboration of my colleague Professor C. R. Hayward. The reading of the page-proof by Professor G. A. Roush detected errata which had escaped my own revision.

H. O. HOFMAN.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
*Boston, Mass., June, 1914.*



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# METALLURGY OF COPPER

## CHAPTER I

### INTRODUCTION

**1. Historical Notice.**<sup>1</sup>—Copper is a widely distributed metal, and next to iron, it is the most important.<sup>2</sup> In prehistoric times it was used for domestic utensils and for implements of war.<sup>3</sup> In the archæological chronology of the stone, bronze, and iron ages, it has been supposed that the use of copper always preceded that of iron; at present it is held that generally iron was converted to use at an earlier period than copper, although in regions in which native copper occurred at the surface it was worked before iron, which had first to be reduced to the metallic state. Thus the races inhabiting this continent<sup>4</sup> before the Indian were acquainted with copper, as is shown by the utensils found in Western mounds. In opening the Lake Superior copper mines, excavations to the depth of 60 ft. were encountered containing stone hammers and charcoal indicating that fire-setting had been the method of winning native copper. At Ducktown, Tenn.,<sup>5</sup> are remains of prehistoric smelting operations.

Copper was mined first in Connecticut (1709), later in New Jersey and Pennsylvania, but no work of any importance was carried on until the middle of the last century. In 1845 the whole output of copper was 100 tons, and this came from Vermont, Pennsylvania, Virginia, North Carolina, and Georgia. California became a producer in 1860. In 1841 the existence of native copper at Lake Superior became generally known, but copper mining as an industry was not established until 1850. Lake Superior was the leading copper producer up to 1887, when it was outranked by Montana, where copper mining began early in the seventies,<sup>6</sup> and smelting about 1880.<sup>7</sup> The third great copper

<sup>1</sup> Beck, L., "Die Geschichte des Eisens," Vieweg, Brunswick, 1891, I, Introduction, p. 17. Agricola—Hoover, "De Re Metallica," London, 1913, p. 402, *Eng. Min. J.*, 1913, xcvi, 359.

<sup>2</sup> Douglas, *Eng. Min. J.*, 1912, xciii, 776.

<sup>3</sup> Garland, "Metallograph. Res. Egyptian Metal Antiquities," *J. Inst. Met.*, 1913, x, 329.

<sup>4</sup> Foster, J. W. and Whitney, J. D., "Report on the Geology and Stratigraphy of Lake Superior," Interior Department Land Office, Washington, 1850 and 1851.

Whitney, J. D., "Metallic Wealth of the United States," Lippincott, Philadelphia, 1854. "Mineral Statistics of Michigan," 1880.

Kirchhoff, "Mineral Resources of the United States," 1882, p. 213. *Tr. A. I. M. E.*, 1876-77, v, 165 (Hewitt); 1890-91, xix, 679 (Douglas); 1906, xxxvii, 288 (Wood, chemical analyses); *Min. Ind.*, 1894, iii, 243 (Douglas, chemical analyses); 1895, iv, 269 (Douglas).

<sup>5</sup> Henrich, *Tr. A. I. M. E.*, 1895, xxv, 175.

<sup>6</sup> Weed, H. V., *Professional Paper* No. 74, U. S. Geol. Survey, 1912.

<sup>7</sup> Hofman, *Tr. A. I. M. E.*, 1904, xxxiv, 258.

district is in the Southwest, including New Mexico, Arizona,<sup>1</sup> and Lower California. The existence of copper in this region was known to the Mexicans,<sup>2</sup> but active operations began after 1880 with the building of the Southern and the Atlantic & Pacific Railroads. In recent years Utah, Nevada, California, and some of the Southern states have entered the list of important producers of the country.

2. **Statistics.**—The world's production<sup>3</sup> of copper in 1912 is given in Table 1, that of the United States<sup>4</sup> in Table 2.

TABLE 1.—WORLD'S PRODUCTION OF COPPER

(In metric tons)

Africa.....	16,633	Mexico.....	73,617
Argentina.....	335	Newfoundland.....	549
Australasia.....	47,774	Norway.....	11,156
Austria.....	4,024	Peru.....	26,483
Bolivia.....	4,681	Russia.....	33,550
Canada.....	34,213	Spain, Portugal.....	59,876
Chile.....	39,204	Sweden.....	1,524
Cuba.....	4,393	Turkey.....	508
Germany.....	24,304	United Kingdom.....	405
Italy.....	2,337	United States.....	563,260
Japan.....	62,486		
		Total.....	1,011,312

TABLE 2.—UNITED STATES' PRODUCTION OF COPPER

(In pounds)

Alaska.....	2,602,000	Nevada.....	82,530,608
Arizona.....	357,952,962	New Mexico.....	27,488,912
California.....	31,069,029	Utah.....	131,673,803
Colorado.....	7,502,000	Wyoming.....	1,121,109
Idaho.....	5,964,542	Southern States.....	18,592,655
Michigan.....	231,628,486	Other States.....	4,396,667
Montana.....	309,247,735		
		Total.....	1,241,762,508

Table 1 shows that the United States produced about 55 per cent. of world's copper. The leading producing states, as given in Table 2, are Arizona, Montana, Michigan, and Utah, which furnish 83 per cent. of the country's product.

There are sold in the American market three grades of copper. The average price of Lake copper in New York for 1912 was 16.56 cents per pound; of electrolytic copper, 16.34 cents; casting copper is usually 1 to 2 cents per pound less than Lake copper. The costs of producing copper in different parts of the United States have been analyzed by Steele.<sup>5</sup> He finds that the average cost for the country lies between 9.6 and 10.0 cents per pound.

<sup>1</sup> Martin, *Eng. Min. J.*, 1913, xcv, 882.

<sup>2</sup> Wendt, *Tr. A. I. M. E.*, 1886-87, xv, 25.

<sup>3</sup> *Min. Ind.*, 1912, xxi, 168.

<sup>4</sup> *Op. cit.*, 160.

<sup>5</sup> *Eng. Min. J.*, 1913, xcvi, 251.

**3. Bibliography.**—The number of books dealing with copper alone is comparatively small, and none of them covers the entire ground. Usually the subject is discussed in treatises on non-ferrous metallurgy. Thus, the works of Percy (1867), Kerl (1881), Balling (1885), Schnabel-Louis (1905), Hildebrandt (1906), and Prost (1912) contain valuable discussions of the subject. There is subjoined a list of books dealing exclusively or mainly with copper.

Grüner, L., "Métallurgie du Cuivre," Paris, 1884.

Howe, H. M., "Copper Smelting," *Bull.* 26, U. S. Geol. Survey, 1885, now out of print.

Peters, E. D., "Modern Copper Smelting," New York, 1895.

Lang, H., "Matte Smelting," New York, 1896.

Peters, E. D., "Principles of Copper Smelting," New York, 1907.

Trochu, P., "Les Pyrites," Paris, 1907.

Hixon, H. W., "Notes on Lead and Copper Smelting and Converting," New York, 1908.

Venancourt, G. C. de, "Le Water-jacket à Cuivre," Paris, 1910.

Peters, E. D., "Practice of Copper Smelting," New York, 1911.

Greenawalt, W. E., "The Hydrometallurgy of Copper," New York, 1912.

Ulke, T., "Modern Electrolytic Copper Refining," New York, 1903.

The subject of copper alloys is not taken up in these works. There exist many valuable monographs and papers on the various phases of the metallurgy of copper; these are referred to in the text.

## CHAPTER II

### PROPERTIES OF COPPER<sup>1</sup>

**4. Physical Properties.**—The metal occurs in the native state. The specific gravity of pure copper at 20° C. is 8.89;<sup>2</sup> good commercial metal shows lower values owing to porosity,<sup>3</sup> the presence of  $\text{Cu}_2\text{O}$ ,<sup>4</sup> and impurities. The specific gravity of molten metal is given as 8.22.

The luster of the compact metal is metallic, while precipitated metal is dull. The color of compact metal is a yellowish-red; it ranges from orange-red to rose-color, the shades being governed by the temperature of the cooling-water in which the casting has been quenched. Metal precipitated from solution is a brownish-red; a colloidal solution has a violet to brownish color.<sup>5</sup> Copper is transparent in thin films transmitting greenish to bluish light.

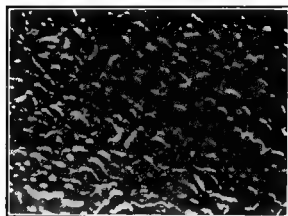


FIG. 1.—Surface of cast copper, 30 diameters.

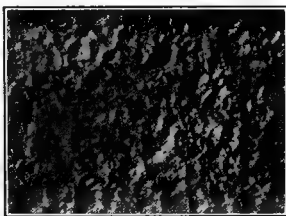


FIG. 2.—Surface of electrodeposited copper, 30 diameters.

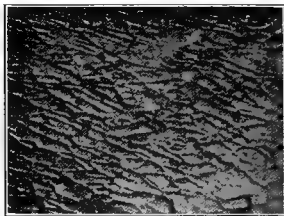


FIG. 3.—Surface of rolled copper, 30 diameters.

Copper crystallizes mainly in isometric forms, and twin crystals are common. Under the microscope<sup>6</sup> the surface<sup>7</sup> of cast copper (Fig. 1) is seen to be made up of large primary grains, composed of small secondary grains with definite orientation; that of electrodeposited copper (Fig. 2), of primary grains only, which have

<sup>1</sup> Hampe, *Zt. Berg. Hütten. Sal. Wesen i. Pr.*, 1873, XXI, 218; 1874, XXII, 93; 1876, XXIV, 6.

<sup>2</sup> Circular 31, Bureau of Standards, 1912, p. 61.

<sup>3</sup> Stahl, *Berg. Hüttenm. Z.*, 1901, LX, 77.

<sup>4</sup> Trippel, *Eng. Min. J.*, 1888, XLV, 436.

<sup>5</sup> Rassenfosse, *J. Soc. Chem. Ind.*, 1911, XXX, 1335.

<sup>6</sup> Baucke, *Proc. Internat. Assoc. Testing Materials*, 1912, II, 14.

Bassett, *Met. Chem. Eng.*, 1913, XI, 64.

<sup>7</sup> Campbell, *Report Alloys Research Comm.*, 1904, p. 867; *J. Frankl. Inst.*, 1902, CLIV, 14; *Metallurgie*, 1907, IV, 828.

Addicks, *Electrochem. Ind.*, 1903, I, 582.

Huntington, *Eng. Min. J.*, 1905, LXXX, 1109; *Metallurgie*, 1906, III, 40.

Abbott, *Eng. Min. J.*, 1909, LXXXVII, 1040.

Faust, *Zt. anorg. Chem.*, 1912, LXXVIII, 201; *J. Inst. Met.*, 1913, IX, 223.

Wäser-Kühml, *Electrochem. Zt.*, 1912, XVIII, 151, 211.



no regular orientation to one another. With rolled copper (Fig. 3), the secondary grains are elongated in the direction in which rolling took place, and this gives the metal the characteristic fibrous structure.<sup>1</sup> The so-called allotropic copper of Schützenberger<sup>2</sup> has been found by Benedicks<sup>3</sup> to consist of ordinary copper containing varying amounts of  $\text{Cu}_2\text{O}$ . The dilatation experiments of Turner and Levy<sup>4</sup> on hard-drawn and annealed wire give simple curves without any jog whatever.

The fracture of cast copper is hackly to granular; that of rolled or drawn copper, fibrous.

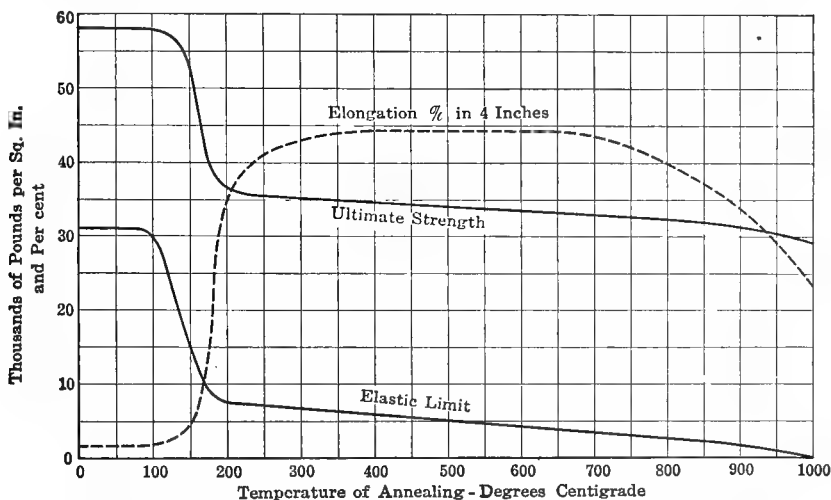


FIG. 4.—Mechanical properties of electrolyte copper as affected by temperature.

Copper is soft when pure; with Fe at 4.5 and Ag at 2.7, the scratch-hardness<sup>5</sup> of Cu is 3.7.

The tensile strength of the cast or hard-drawn metal is 60,000–70,000 lb. per square inch; annealing reduces it to 30,000–40,000 lb.<sup>6</sup> Shock-tests by Baucke<sup>7</sup> show that cast copper has a very low resilience, and that the property is improved by forging. A rise in temperature weakens the metal.<sup>8</sup> Fig. 4,

<sup>1</sup> Robin, "Annealing of Copper," *Rev. Mét.*, 1913, x, 750.

<sup>2</sup> *Compt. rend.*, 1887, LXXXVI, 1240, 1397.

<sup>3</sup> *Metallurgie*, 1907, iv, 5, 33.

<sup>4</sup> *Proc. Roy. Soc., Ser. A.*, 1907, LXXX, 1; *Rev. Mét. Extr.*, 1908, LV, 655.

<sup>5</sup> Martens, *Mitth. Kgl. techn. Versuchsanst.*, 1894, XVI, 172; *Iron Age*, 1894, LIV, 900.

<sup>6</sup> Bennet, "Tensile Strength of Electrolytic Copper," *Tr. Am. Electro. Chem. Soc.*, 1912, XXI, 243. *Met. Chem. Eng.*, 1912, x, 298.

<sup>7</sup> *Internat. Zt. Metallographie*, 1912, III, 195; *J. Inst. Met.*, 1913, IX, 210.

<sup>8</sup> Gard, *Rev. Mét.*, 1909, VI, 1069.

Leidig, *Verh. Ver. Beförd. Gewerbebl.*, 1911, XC, 459, 525.

Johnson, *Met. Chem. Eng.*, 1911, IX, 399.

Huntington, *J. Inst. Met.*, 1912, VIII, 127.

Müller, *Metall-Erz*, 1913, X, 220.

by Grard, shows the mechanical changes electrolytic copper undergoes with a rise in temperature.

The pure metal is easily rolled into sheets,<sup>1</sup> hammered into foil<sup>2</sup> and drawn into fine wire.<sup>3</sup> The hardness caused by mechanical treatment is removed by

annealing<sup>4</sup> at a temperature ranging from 500° to 700° C. in an atmosphere free from S.<sup>5</sup>

Welding<sup>6</sup> by ordinary means is possible to small extent; pieces are easily joined by electric welding.

Molten copper absorbs<sup>7</sup> SO<sub>2</sub>, H, and CO (disputed by Sieverts), but no C<sub>x</sub>H<sub>y</sub>; upon solidification most of the absorbed gases are given off, at least at atmospheric pressure.<sup>8</sup> The absorbing power rises with the

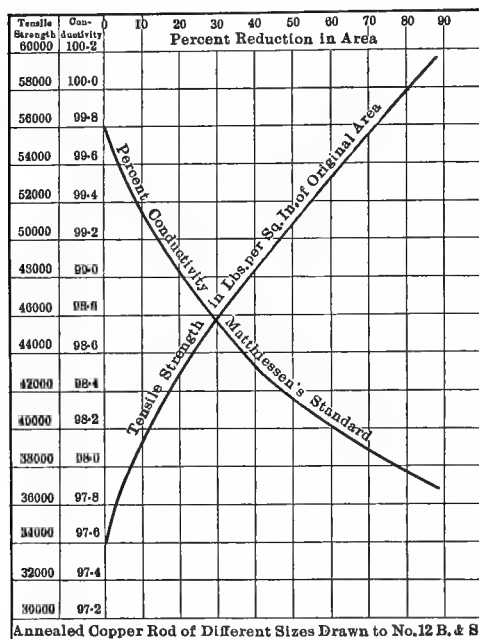


FIG. 5.—Electric conductivity of copper as affected by mechanical treatment.

<sup>4</sup> Howe, *Tr. A. I. M. E.*, 1884-85, XIII, 646.

Cummins, *Eng. Min. J.*, 1890, I, 216.

Thomas, *Iron*, 1892, XL, 399.

Heyn, *J. I. and St. I.*, 1902, II, 745.

Stahl, *Metallurgie*, 1908, V, 289.

<sup>5</sup> Johnson, *Met. Chem. Eng.*, 1911, IX, 187.

<sup>6</sup> Waite, "Leibe Process," *Eng. Min. J.*, 1890, LXIX, 705.

McRoberts, "Birmingham Process," *Iron Age*, 1891, XLVIII, 1156.

<sup>7</sup> Caron, *Compt. rend.*, 1866, LXIII, 1129.

Hampe, *Zt. Berg. Hütten. Sal. Wesen i. Pr.*, 1873, XXI, 274; *Chem. Z.*, 1886, XVII, 1692.

Stahl, *Berg. Hüttenm. Z.*, 1886, XLV, 414; 1889, XLIX, 299; 1893, LII, 19; 1901, LX, 77.

*Metallurgie*, 1907, IV, 761.

Sieverts, *Ber. deutsch. chem. Ges.*, 1910, XLIII, 893; 1912, XLV, 221; *Zt. Electrochem.*, 1910, XVI, 707; *Zt. phys. Chem.*, 1911, LXXVII, 591.

Guichard, *Compt. rend.*, 1911, CLIII, 104; *J. Inst. Met.*, 1911, VI, 329.

<sup>8</sup> SO<sub>2</sub>: Schenck-Hempelmann, *Metall-Erz*, 1913, X, 28.

Stubbs, *J. Soc. Chem. Ind.*, 1913, XXXII, 311.

<sup>1</sup> Powe, *Brass World*, 1909, I, 183.

Copperman, *Met. Ind.*, 1909, VII, 4, 64, 99, 134.

<sup>2</sup> Fuller, J., "Art of Copper Smithing," Spon, London, 1912.

<sup>3</sup> Küpper, *Zt. Verein deutsch. Ing.*, 1906, I, 1899, 2022; *Rev. Mét. Extr.*, 1907, IV, 722.

Pye, *J. Inst. Met.* 1911, VI, 165; *Circular No. 31*, "Copper Wire Tables," Bureau of Standards, 1912.

temperature, and is interfered with by  $\text{Cu}_2\text{O}$ , P, As, and Sb. At a red heat copper readily absorbs H.<sup>1</sup>

The melting point of copper is  $1083^\circ\text{C}$ .; the latent heat of fusion 43.3 cal.; the boiling point  $2310^\circ\text{C}$ .<sup>2</sup> *In vacuo* volatilization<sup>3</sup> is noticeable at  $700^\circ$  and decided near the melting point.<sup>4</sup> When volatilized by heating with the oxyhydrogen blowpipe or the electric arc, it burns with a green flame; the fumes are poisonous.<sup>5</sup> The specific heat at  $170^\circ\text{C}$ . is 0.09244; at  $100^\circ$ , 0.09422;

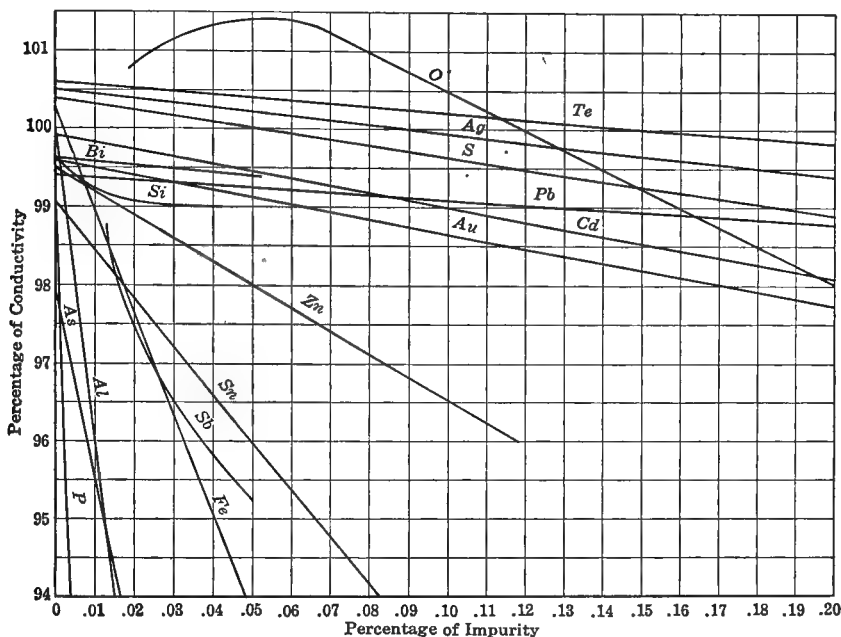


FIG. 6.—Electric conductivity of copper as affected by impurities.

at  $300^\circ$ , 0.09846. The coefficient of linear expansion is 0.00017. The thermal conductivity is 736 when  $\text{Ag}=1000$ , or 0.72 g. cal. per degree centigrade for a cube whose side is 1 cm.

The electric conductivity<sup>6</sup> of 1 cm. cube at  $0^\circ\text{C}$ . = 620,000 reciprocal ohms;

<sup>1</sup> Heyn, *Zt. Ver. deutsch. Ing.*, 1900, XLIV, 508; *Metallographist*, 1903, VI, 48; *Metallurgie*, 1906, III, 82.

Sieverts, *Zt. phys. Chem.*, 1911, LXXVII, 591; *J. Inst. Met.*, 1911, VI, 342.

Heath, "Estimation of Oxygen and Occluded Gases in Copper," *J. Ind. Eng. Chem.*, 1912, IV, 402.

<sup>2</sup> Greenwood, *Eng. Min. J.*, 1911, XCII, 3.

<sup>3</sup> Hughes, *J. Inst. Met.*, 1912, VII, 700.

<sup>4</sup> Kahlbaum, *Berg. Hüttenm. Z.*, 1898, LVII, 201; 1902, LXI, 295.

<sup>5</sup> Hansen, *Met. Chem. Eng.*, 1911, IX, 67.

<sup>6</sup> Wolff, F. A., and Dellinger, J. H., Bureau of Standards, VII, No. 1 (reprint No. 148), 1911: "The Electric Conductivity of Commercial Copper."

Northrup, Resistivity between 20 and  $1450^\circ\text{C}$ ., *J. Franklin. Inst.*, 1914, CLXXVII, 1.

or the resistance of a wire 1 ft. long and 0.001 in. in diameter at  $0^{\circ}\text{C.} = 9.529$  ohms for annealed and 9.71 for hard-drawn wire. The conductivity of cast copper is about 3.5 per cent. lower than that of annealed wire. In smelting works the conductivity is usually given in terms of the Mathiessen Standard. This standard is equal to copper which at  $15^{\circ}\text{C.}$  has a resistance of 1687 reciprocal ohms per cubic centimeter, or 1 meter-gram of pure soft copper at  $0^{\circ}\text{C.} = 0.14172$  international ohm. The standard is represented by the figure 100; cathode copper not melted has shown 103.14; mass copper from Lake Superior 102.5; electrolytic wire bar often reaches 101; Lake copper usually is 99.<sup>1</sup> Tests are usually made on annealed wire, No. 12 B. & S. gauge ( $= 0.08081$  in. in diameter). The conductivity as affected by mechanical treatment is shown in the diagram of Addicks<sup>2</sup> (Fig. 5). If the conductivity is to be given for hard-drawn

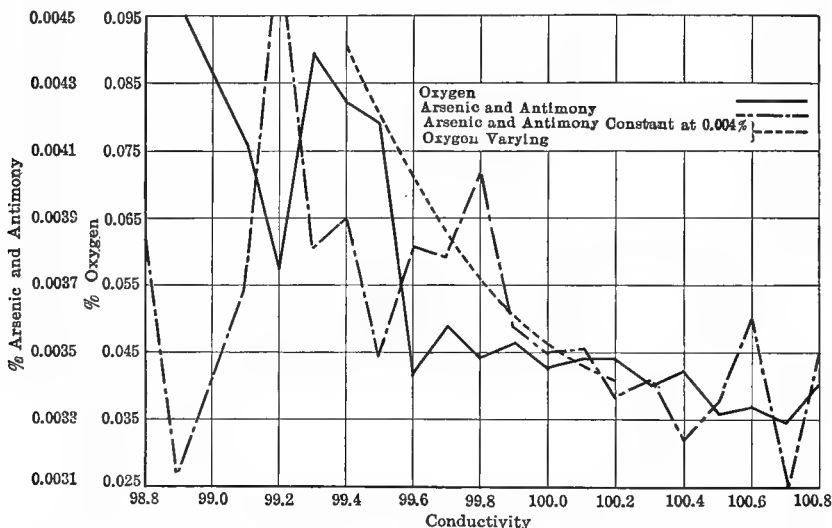


FIG. 7.—Electric conductivity of copper as affected by Oxygen, Arsenic and Antimony, severally and combined.

wire, it is customary to deduct 2.5 per cent. from the figure obtained with annealed wire. Small amounts of impurity have a decided influence upon the conductivity of copper. Fig. 6 gives some of the experimental results of Addicks.<sup>3</sup> Arsenic and antimony are the two impurities likely to be found in refined copper which strongly depress the electric conductivity; thus 0.0013 per cent. As<sup>4</sup> or 0.0071 per cent. Sb lower it 1 per cent., while the elements

<sup>1</sup> Table II, Wolff-Dellinger, *op. cit.*

<sup>2</sup> *Electrochem. Ind.*, 1903, I, 581.

<sup>3</sup> *J. Frankl. Inst.*, 1905, CLX, 425; *Tr. A. I. M. E.*, 1906, XXXVI, 18. Other data: Keller, *Min. Ind.*, 1898, VII, 243, complete analyses with tensile strengths and electric conductivities.

<sup>4</sup> Hiorns-Lamb, *J. Soc. Chem. Ind.*, 1909, XXVIII, 451, curve 1-3 per cent. As.

Friedrich, *Metallurgie*, 1908, V, 533, curve 1-12 per cent. As.

Puschin-Dischler, *Am. Chem. Soc. Chem. Abstracts*, 1912, VI, 1587; *Zi. anorg. Chem.*, 1913, LXXX, 65, curve 1-45 per cent. As.

which render copper brittle appear to have little effect upon the electric properties.<sup>1</sup> Fig. 7 shows the combined effects of As and Sb in Montana electrolytic copper within a range of 0.0034 and 0.0044 per cent. The curve for O in Fig. 4 is abnormal, because  $\text{Cu}_2\text{O}$  reduces the conductivity progressively.<sup>2</sup> It finds its probable explanation in the circumstance that O introduced as  $\text{Cu}_2\text{O}$  or  $\text{CuO}$  into the Cu, oxidizes the slight amount of impurity present in high-grade metal and thus increases the conductivity of the latter. The behavior of a small amount of impurity depends greatly upon the form in which it is present; if in the metallic state, it is liable to form a solid solution with the Cu, and have a greater depressing effect than if present in some other form. Such irregularities are well brought out in Fig. 7.

Copper is diamagnetic.

**5. Chemical Properties.**—At ordinary temperature copper is not attacked by dry air nor by moist air free from  $\text{CO}_2$ ; in the presence of this gas it becomes coated with a green basic carbonate.<sup>3</sup> The chemical theory of corrosion has been in part replaced by the electrolytic theory.<sup>4</sup> When heated above  $185^\circ\text{C}$ . copper begins to oxidize, becomes rose-colored at about  $200^\circ$ , brass-colored at  $300^\circ$ , bluish-green at  $350^\circ$ , and dark above that temperature. At a red heat it becomes coated with a dark scale consisting on the outside of  $\text{CuO}$  and on the inside of  $\text{Cu}_2\text{O}$ ; the scale is separated from the metal by bending and quenching. According to Heyn<sup>5</sup> copper heated for a short time above  $500^\circ\text{C}$ . withstands a smaller number of bends than when heated below this temperature because of the  $\text{Cu}_2\text{O}$  that has been formed. It is clear that overheating<sup>6</sup> a cake of copper which causes a superficial oxidation will affect the sheet that is rolled from it.

Copper is readily soluble in  $\text{HNO}_3$ , when not too concentrated; in *aqua regia*; boiling  $\text{H}_2\text{SO}_4$  of  $66^\circ\text{Bé}$ ; slowly soluble in hot dilute  $\text{H}_2\text{SO}_4$  in the presence of air; in dilute  $\text{HCl}$  with air; in  $\text{NH}_4\text{OH}$  with air; in  $\text{KCN}$  with or without air;  $\text{H}_2\text{SO}_3$  slowly changes Cu into  $\text{CuS}$ .

<sup>1</sup> Bardwell, *Tr. A. I. M. E.*, 1913, XLVI.

<sup>2</sup> Walker, *Min. Ind.*, 1898, VII, 248.

Hofman-Hayden-Hallowell, *Tr. A. I. M. E.*, 1907, XXXVIII, 178, 183.

<sup>3</sup> Diegel, *Zt. Verein Bf. Gewerbeft.*, 1899, LXXVIII, 313; 1903, LXXX, 93, 119, 157.

Heyn, *Mitth. Kgl. Materialprüfungsanstalt*, 1911, XXIX, 29.

Eastick, *Met. Ind.*, 1913, XI, 524.

<sup>4</sup> Bengough, *J. Inst. Met.*, 1911, V, 28.

Philip, *op. cit.*, 1912, VII, 50; 1913, IX, 61.

<sup>5</sup> *Mitth. Kgl. techn. Versuchsanst.*, 1900, XVIII, 327; *Zt. Ver. deutsch. Ing.*, 1902, XXXVI, 1119; *Stahl u. Eisen*, 1902, XXII, 1234.

<sup>6</sup> Stahl, *Metallurgie*, 1908, V, 289; 1912, IX, 418.

## CHAPTER III

### COPPER OF COMMERCE, ITS IMPURITIES AND THEIR EFFECTS

**6. Grades of Copper.**<sup>1</sup>—In the United States there are marketed three grades of copper: electrolytic, Lake, and casting copper, which are cast in the forms of wire bar, ingot and ingot bar, and cake. Electrolytic and Lake copper contain over 99.8 per cent. Cu; casting copper as little as 98.5 per cent. Cu. According to tests made by W. H. Bassett<sup>2</sup> in 1903-04 an average of 511 samples of best electrolytic copper gave on hard-drawn wire 0.003 in. in diameter, tensile strength 65,259 lb. per square inch, and elongation 1.55 per cent. in 8 in.; on annealed wire, 0.06 in. in diameter, in 6 in. 24.8 twists and 13.6 bends; electric conductivity 100.32 per cent. Math. Stand. An average of 55 samples of best Lake copper gave tensile strength 66,141 lb., elongation 1.45 per cent., twists 22.2, bends 12.2, conductivity 99.85 per cent. Thus as regards physical properties electrolytic copper is preferable to Lake copper. If, nevertheless, Lake copper<sup>3</sup> has been sold at  $\frac{1}{4}$  cent per pound more than electrolytic, the reason is to be found in the uniform character of Lake copper and the irregularities in the properties of electrolytic copper. The tests of Bassett show that the progress made in the electrolytic process and in the fire-refining of cathodes has so improved the character of electrolytic that it stands higher to-day than Lake copper.

Casting copper is a general term for fire-refined blister copper too low in precious metals to make their recovery profitable, and carrying impurities in too small a quantity to make them objectionable. Its electric conductivity is too low to make it available for electric use, and the amount of impurity too high for making brass that is to be rolled or drawn; it serves therefore for making brass and copper castings. Table 3 gives the forms in which copper was cast in the United States in 1911.<sup>4</sup>

TABLE 3.—FORMS IN WHICH COPPER WAS CAST IN THE U. S. IN 1911

Form	Pounds	Per cent.
Wire bars.....	731,029,349	50
Ingot and ingot bars.....	409,786,682	29
Cakes.....	143,716,125	10
Cathodes.....	135,499,770	9
Other forms.....	25,774,328	2
Total.....	1,445,806,254	100

<sup>1</sup> Ingalls, *Eng. Min. J.*, 1912, XCIII, 887, 939, also selling of copper.

Tassin, *Met. Ind.*, 1912, X, 275, 335, 447.

<sup>2</sup> *Records*, Circuit Court of the U. S., Bigelow vs. Calumet & Hecla Mining Co., October 17, 1907.

<sup>3</sup> *Eng. Min. J.*, 1908, LXXXVI, 842.

<sup>4</sup> *Min. Res. U. S.*, 1911, I, 311.

USES OF COPPER.—Metallic copper is used in the arts for electrical purposes, and for the manufacture of brass, bronze, and other alloys; it is rolled into sheets and tubings, and formed into castings. Table 4 gives the distribution of copper in the metal arts in 1907.<sup>1</sup>

TABLE 4.—USES OF COPPER IN THE U. S. IN 1907

Use	Pounds	Per cent.
Electric purposes, including wire.....	228,000,000	41.8
Brass manufacture.....	156,000,000	28.6
Rolling mills, sheet copper.....	34,000,000	6.3
Miscellaneous use, principally castings and alloys.....	127,000,000	23.3
Total.....	645,000,000	100.0

SPECIFICATIONS.—The standard specifications for copper-wire bars, cakes, slabs, billets, ingots, and ingot bars adopted by the American Society of Testing Materials, August 21, 1911,<sup>2</sup> are given in the following:

1. (a) METAL CONTENTS.—The copper in all shapes shall have a purity of at least 99.88 per cent. as determined by electrolytic assay, silver being counted as copper.

(b) CONDUCTIVITY.—All wire bars shall have a conductivity of at least 98.5 per cent. (annealed); all ingots and ingot bars shall have a conductivity of at least 97.5 per cent. (annealed), excepting only arsenical copper, which shall have a conductivity of not less than 90 per cent. (annealed).

Cakes, slabs, and billets shall come under the ingot classification, except when specified for electrical use at time of purchase, in which case wire-bar classification shall apply.

The "Annealed copper standard," or resistance of a meter-gram of standard annealed copper at 20° C., shall be considered as 0.15302 international ohm. The per cent. conductivity for purposes of this specification shall be calculated by dividing the resistivity of the annealed copper standard by the resistivity of the sample at 20° C.

2. Wire bars, cakes, slabs, and billets shall be substantially free from shrink holes, cold sets, pits, sloppy edges, concave tops, and similar defects in set or casting. This clause shall not apply to ingots or ingot bars, in which case physical defects are of no consequence.

3. Five per cent. variation in weight or  $\frac{1}{4}$  in. variation in any dimension from the refiner's published list or purchaser's specified size shall be considered good delivery; provided, however, that wire bars may vary in length 1 per cent. from the listed or specified length, and cakes 3 per cent. from the listed or specified size in any dimension greater than 8 in. The weight of ingot and ingot-bar copper shall not exceed that specified by more than 10 per cent., but otherwise its variation is not important.

The specifications of the leading copper producers of the world are contained in the report made by Guillet<sup>3</sup> at the Copenhagen Congress. The congress

<sup>1</sup> *Min. Res. U. S.*, 1907, I, 639.

<sup>2</sup> *Year-book*, 1911, p. 127.

<sup>3</sup> *Rev. Mét.*, 1909, VI, 1245.

of New York in 1912<sup>1</sup> has only laid out a program for future work. Considering that 95 per cent. of United States copper is made up of electrolytic and Lake brands, both more than 99.8 per cent. pure, the choice of electric conductivity as standard for quality is to be expected. This standard, however, is not suited to most European brands which contain less than 99.8 per cent. Cu, but have excellent wearing qualities owing to the presence of As, Sb, Ni, etc.<sup>2</sup>

**7. Impurities and Their Effects in General.**<sup>3</sup>—Copper of commerce, as stated above, is not pure. It contains Cu<sub>2</sub>O and foreign metals and their oxides which affect the physical and chemical properties, and thereby the availability for use in the arts. Table 6 gives typical chemical analyses of some leading brands of to-day. They show that the copper produced at present is of a higher grade than that of former years, when copper contents of 97–98 per cent. were not uncommon.<sup>4</sup> The total impurity in copper is small, but the number of elements composing it is large; and a small percentage of a single element may

TABLE 5.—CHEMICAL ANALYSIS OF REFINED COPPER

Element	Lake, wire bar <sup>1</sup>	Lake, arsenical, ingot <sup>1</sup>	Electrolytic, wire bar <sup>1</sup>				Best selected English <sup>1</sup>
Cu+Ag.....	99.900	99.4385	99.970	99.895	99.9548	99.9780	99.5510
Cu.....	99.890	99.4131	99.967	99.893	99.953	99.976	99.530
Ag.....	0.0096 (2.8 oz.)	0.0254 (7.41 oz.)	0.0027 (0.79 oz.)	0.0020	0.0018	0.0020	0.0210
Pb.....	2.0031	0.0027	0.0024	0.0072	0.0010	0.0056	0.1331
Bi.....	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
As.....	0.0062	0.3183	0.0006	0.0001	0.0000	0.0001	0.0071
Sb.....	0.0000	0.0000	0.0000	0.0006	0.0009	0.0008	0.0087
Se+Te.....	0.0020	n. d.	0.0000	0.0022	0.0026	0.0014	0.0066
Fe.....	0.0028	0.0056	0.0023	0.0028	0.0038	0.0044	0.0044
Ni.....	0.0090	0.0153	0.0030	0.0010	0.0028	0.0018	0.1112
Zn.....	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
S.....	0.0016	0.0071	0.0026	0.0023	0.0026	0.0016	0.0074
O (by diff.).....	0.0753	0.2143	0.0191	0.0888	0.0315	0.0063	0.1705
Sn.....							
Conductivity, annealed.....	96.49		100.84	99.78	100.45	1.0070	
Conductivity, hard drawn....	93.84		97.93	96.65	97.64	97.93	
Difference due to hard drawing.....	2.65		2.91	3.13	2.81	2.77	
Tensile strength, lb. sq. in....	67,590		65,000	67,800	66,300	66,550	
Twists in 6 in.....	17		18	27	34	53	
Elongation per cent.....	103*		1.65*	1.15†	1.04†	1.08†	
Bends, annealed.....	11		14	14	14	22	
Diam. of wire, in.....	0.080		0.080	0.080	0.080	0.080	

\* In 8 in. † In 60 in.

<sup>1</sup> W. H. Bassett.

<sup>1</sup> Guillet, *op. cit.*, 1912, IX, 1037.

<sup>2</sup> Lewis, *Met. Chem. Eng.*, 1912, X, 540.

<sup>3</sup> Hampe, *loc. cit.*

Greaves, *J. Inst. Met.*, 1912, VII, 218.

Archbutt, *op. cit.*, 1912, VII, 262.

Johnson, *op. cit.*, 1912, VIII, 192; 1913, X, 275.

Law, *op. cit.*, 1912, VIII, 222.

Tassin, *Met. Ind.*, 1912, XVIII, 275, 335, 447.

Lewis, *Met. Chem. Eng.*, 1912, X, 540.

Baucke, *Int. Zt. Metallographie*, 1913, III, 195.

<sup>4</sup> Kerl, B., "Metallhüttenkunde," Leipzig, 1881, pp. 189, 200, 221.



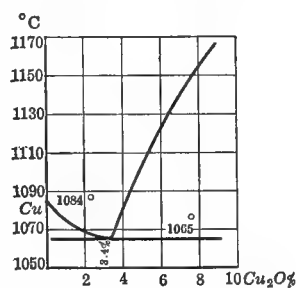
TABLE 5.—CHEMICAL ANALYSIS OF REFINED COPPER (Continued)

Element	Casting copper <sup>6</sup>	Casting copper <sup>2</sup>	Lake <sup>3</sup>			Merchant bar, England <sup>4</sup>	Oker, Germany <sup>5</sup>	Wallaroo, Australia <sup>1</sup>	Mansfeld, Germany <sup>5</sup>
Cu+Ag	.....	99.45	99.950	99.930	99.935	99.904	99.397	99.648	99.6417
Cu	99.50	99.44	99.879	99.873	99.867	99.870	99.395	.....	99.6125
Ag	.....	0.01	0.071	0.057	0.068	0.034	0.072	.....	0.0292
Pb	0.05	.....	.....	trace	0.0011	.....	0.061	.....	0.020
Bi	.....	0.01	.....	.....	.....	.....	0.052	.....	.....
As	.....	0.02	0.0006	0.0099	0.0004	0.002	0.135	trace	0.0172
Sb	.....	0.05	trace	trace	trace	.....	0.095	0.0007	0.0023
Se+Te	.....	.....	.....	.....	.....	.....	.....	.....	.....
Fe	0.06	0.38	0.0014	0.0063	0.0027	0.011	0.063	.....	0.0039
Ni	0.15	.....	0.0010	0.0108	trace	.....	0.064	0.237	0.2112
Zn	.....	.....	trace	0.0008	0.0005	0.013	.....	.....	.....
S	.....	0.002	0.0022	0.0064	0.0006	.....	0.001	.....	0.0024
O	trace	.....	0.045	0.056	0.064	0.068	0.1166	.....	0.00752 <sup>†</sup>
Sn	0.18	.....	.....	.....	.....	.....	.....	.....	.....
Conductivity, annealed	.....	.....	101.0	95.7	101.1	.....	Co 0.012	.....	.....

have a very decided influence upon the properties. The presence of two foreign substances in copper may intensify their respective harmful effects, or may neutralize them; they may also act independently and interfere with one another.

**8. Oxygen.**<sup>1</sup>—Oxygen is insoluble in copper. Nearly all the O is present as Cu<sub>2</sub>O, which is the only copper oxide stable at the melting point of copper.

Slade-Farrow<sup>2</sup> found that a mixture of Cu and Cu<sub>2</sub>O liquefied at 1195° C. and separated into two layers containing respectively 20 and 95 per cent. Cu<sub>2</sub>O. The equilibrium diagram of the Cu-Cu<sub>2</sub>O series of alloys by Heyn<sup>3</sup> is given in Fig. 8. It has the characteristic V-shaped form of an alloy forming a eutectic mixture. The eutectic contains 3.45 per cent. Cu<sub>2</sub>O and solidifies at 1064° C.<sup>4</sup> In fire-refining copper (§ 186) the metal is saturated with Cu<sub>2</sub>O to form the so-called set-copper containing about 6 per cent. Cu<sub>2</sub>O, while refined copper contains 0.5± per cent.

FIG. 8.—Alloy-series Cu-Cu<sub>2</sub>O

Cu<sub>2</sub>O, the amount varying with the pitch (ingot-, wire- bar, plate-) to which

† Determined.

<sup>1</sup> W. H. Bassett.

<sup>2</sup> *Brass World*, 1905, I, 95.

<sup>3</sup> J. B. Cooper, Private communication.

<sup>4</sup> *Electrical Review*, March 3, 1897, p. 101.

<sup>5</sup> *Zt. Berg. Hütten. Sal. Wes., i. Pr.*, 1873, XXI, 252, 254.

<sup>6</sup> Bay-Plant, Balbach S. & R. Co., Newark, N. J.

Great Falls, Mont., "Electrolytic Wire Bar," Burns, *Tr. A. I. M. E.*, 1913, XLVI.

Collections of other analyses: Keller, *Min. Ind.*, 1898, VII, 243.

Holland-Bertiaux, *Rev. Mét.*, 1906, III, 205.

<sup>1</sup> See also Refining Copper, § 186.

<sup>2</sup> *Proc. Roy. Soc. A.*, 1912, LXXXVII, 524; *J. Inst. Met.*, 1913, IX, 207; *Met. Chem. Eng.*, 1913, XI, 165; *Zt. Electrochem.*, 1912, XVIII, 817.

<sup>3</sup> *Milth. Kgl. Versuchsanst.*, 1900, XVIII, 315; *Metallographist*, 1903, VI, 49; *Tr. A. I. M. E.*, 1904, XXXIV, 677.

<sup>4</sup> Dejean, *Rev. Mét.*, 1906, III, 233; reply by Heyn, p. 543.

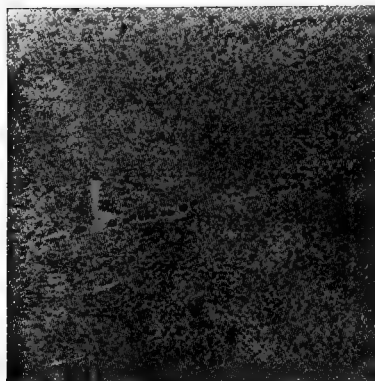


FIG. 9.

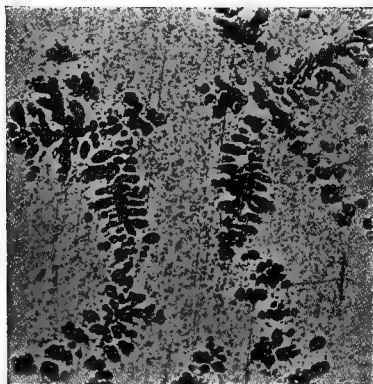


FIG. 10.

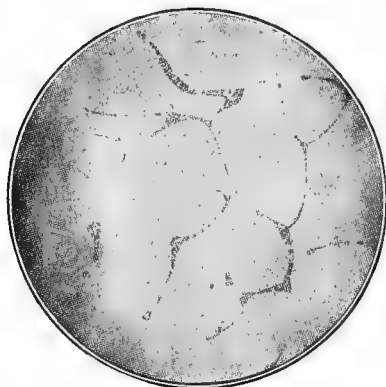


FIG. 11.

FIGS. 9-11.—Three stages in fire-refining of copper

the copper has been poled and with the character of the impurities present. Figs. 9-11 are photomicrographs<sup>1</sup> of cathode copper in three stages of fire-refining. Fig. 9 represents the cathode copper, after melting down, with about 3 per cent  $\text{Cu}_2\text{O}$ ; Fig. 10 set copper with 6.16 per cent.  $\text{Cu}_2\text{O}$ ; and Fig. 11, wire-bar copper with 0.51 per cent.  $\text{Cu}_2\text{O}$ .<sup>2</sup> The amount of  $\text{Cu}_2\text{O}$  present in copper containing less than 3.45 per cent.  $\text{Cu}_2\text{O}$  can be readily found by measuring on an enlarged photomicrograph with a planimeter the Cu areas in a given area, deducting them from the total area, which leaves the eutectic area, and calculating in this the percentage of  $\text{Cu}_2\text{O}$ . With a little practice close valuations can be made by examining a polished surface with the microscope, an operation which takes from 6 to 8 minutes.<sup>3</sup>

The method of Hofman-Green-Yerxa has been modified by Huntington-Desch<sup>4</sup> to secure greater accuracy, and much simplified by Bardwell.<sup>5</sup> The latter projects the image upon Duplex paper so as to cover a circle 15 to 16 in. in diameter, traces the outline with a hard pencil, cuts out the copper areas, weighs them and the residual net-work of eutectic on a chemical balance, and computes the O. From 4 to 5 determinations are made in one hour, and the results check closely.

The  $\text{Cu}_2\text{O}$  in Cu is not reduced by either As or Sb, but readily so by Sn, Zn, Mg, and Pb.<sup>6</sup>

<sup>1</sup> Hofman, Green, Yerxa, *Tr. A. I. M. E.*, 1904, xxxiv, 682; see also Stahl, *Metallurgie*, 1909, IV, 609.

<sup>2</sup> Giraud, *Rev. Mét.*, 1905, II, 297; *Eng. Min. J.*, 1905, LXXX, 170.

<sup>3</sup> Hofman, Green, Yerxa, *Tr. A. I. M. E.*, 1904, xxxiv, 671, 984.

<sup>4</sup> *Tr. Faraday Soc.*, 1908, IV, 51.

<sup>5</sup> *Tr. A. I. M. E.*, 1913, XLVI.

<sup>6</sup> Jolibois-Thomas, *Rev. Mét.*, 1913, X, 1264.

The tensile strength of copper begins to be affected by 0.45 per cent.  $\text{Cu}_2\text{O}$ , but not the malleability; this begins to diminish with 0.9 per cent.  $\text{Cu}_2\text{O}$ .

**9. Lead.**—The constitution of the Cu-Pb alloy series has been investigated by Roberts-Austen,<sup>1</sup> Heycock-Neville,<sup>2</sup> Hiorns,<sup>3</sup> Friedrich-Leroux,<sup>4</sup> and Giolitti-Marantonio.<sup>5</sup> In Figs. 12-12a (Friedrich-Leroux), in area Cu 65 Pb, there are formed, upon cooling, crystals of Cu and mother metal; in that of 1CV crystals of Pb and mother metal; below the eutectic line and to the right of *f*, crystals of Cu and eutectic; and to the left, crystals of Pb and eutectic. Alloys lying between 100 and 65 per cent. Cu form homogeneous solutions above the liquidus, 1084 to about 950° C.; as soon as the temperature reaches line Cu-65, crystals of Cu separate and continue to do this until the point 65 per cent.

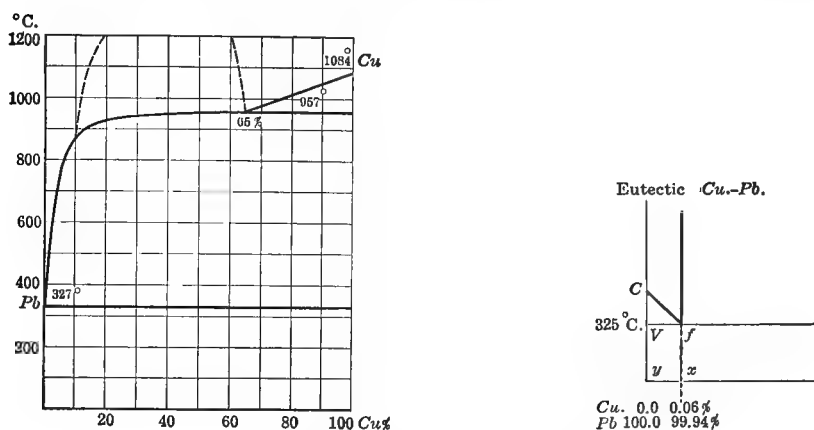


FIG. 12-12a.—Alloy-series Cu-Pb.

Cu has been reached. With a further withdrawal of heat the temperature does not fall, but is kept constant by further separations of Cu until the composition of 65 per cent. Cu—35 per cent. Pb has been changed to that of 10 per cent. Cu—90 per cent. Pb; only now, after the complete disappearance of the former, does the temperature fall with further separations of Cu until the eutectic point *f* (0.06 per cent. Cu, 99.94 per cent. Pb) has been reached with 325° C., when complete solidification takes place. It is thus seen that in Cu, when cooled slowly, there will be found a little Pb, and in Pb a little Cu. If mixtures within the range of 10 and 65 per cent. Cu, or 90 and 35 per cent. Pb, are heated above 1025° C., thoroughly stirred and poured into a chilled mold, an apparently homogeneous alloy will be obtained, which in reality is a conglomerate. Recent investigations by Friedrich-Waehlert<sup>6</sup> have fixed the critical temperature of

<sup>1</sup> 4th Report Alloys Research Committee, 1897, 51.

<sup>2</sup> *Philos. Trans. A.*, 1897, XLII, 189.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1906, XXV, 618.

<sup>4</sup> *Metallurgie*, 1907, IV, 299.

<sup>5</sup> Guertler, "Metallographie," I, part 1, p. 597.

<sup>6</sup> *Metall-Erz*, 1913, X, 578.

the saturation-point curve between 65 and 10 per cent Cu at 1025° C. with the critical point at about 35 per cent. Cu.

The color of the alloys is a reddish gray.

The effect of Pb upon the mechanical properties of Cu depends to a certain extent upon the amount of O present,<sup>1</sup> as the less the O, the smaller is the Pb permissible, because Pb reduces Cu<sub>2</sub>O.<sup>2</sup> Thus O-free Cu with 0.05 per cent. Pb is red-short, while O-bearing Cu can stand as much as 0.2 per cent. and be worked cold or hot; Cu can contain as much as 0.675 Pb<sub>3</sub>As<sub>2</sub>O<sub>8</sub> or 1.45 per cent. 2Cu<sub>2</sub>O.PbO and be only just red-short (Hampe). Jolibois-Thomas<sup>3</sup> have shown that As neutralizes the harmful effect of Pb, in that Pb forms a solid solution with Cu<sub>3</sub>As. Ordinarily it is held that Pb, not to exceed 0.1 per cent., makes Cu roll better, and that 0.2 per cent. makes it brittle.<sup>4</sup> Forging tests of Archbutt<sup>5</sup> showed that 0.2 per cent. Pb did not interfere with working at a red heat.

**10. Bismuth.**—Freezing-point curves have been drawn by Roland-Gosselin,<sup>6</sup> Hiorns,<sup>7</sup> Jeriomin,<sup>8</sup> and Portevin.<sup>9</sup> The curve of Portevin resembles that of Jeriomin. This has the V-shaped form of the eutectic with the eutectic point lying at 0.25 per cent. Bi, and the eutectic line extending to the borders of the diagram. As little as 0.02 per cent. Bi, which is mostly present in the metallic state, makes Cu red-short (Hampe). Baucke<sup>10</sup> found that 0.025 per cent. makes it brittle at a red heat, 0.05 per cent. makes it cold-short,<sup>11</sup> 0.1 per cent.<sup>12</sup> very brittle (Hampe). Lawrie<sup>13</sup> found that Cu with over 0.0005 per cent. Bi could not be drawn into wire. As<sup>14</sup> and Sb<sup>15</sup> counteract to some extent the bad effect of Bi.<sup>16</sup> It is generally accepted that Bi<sub>2</sub>O<sub>3</sub> is less injurious than Bi; Cu<sub>2</sub>O.Bi<sub>2</sub>O<sub>3</sub> less than Bi<sub>2</sub>O<sub>3</sub>, and that Bi<sub>2</sub>O<sub>3</sub>.xSb<sub>2</sub>O<sub>5</sub> can be present to the extent of 0.7 per cent. without producing either cold- or hot-shortness. The alloys are coarsely granular and have a strong luster.

**11. Iron.**—The only freezing-point curve drawn is that of Sahmen.<sup>17</sup> It appears to show that Cu and Fe form heterogeneous mixtures excepting at the

<sup>1</sup> Westmann, *Oest. Zt. Berg. Hüttenw.*, 1903, II, 655.

<sup>2</sup> Jolibois-Thomas, *Rev. Mét.*, 1913, X, 1264.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> Lewis, *Engineering*, 1903, LXXVI, 753; *Eng. Min. J.*, 1904, LXXVII, 284; *Am. Mfr.*, 1903, LXXIII, 903; *Min. Ind.*, 1903, XII, 127; *Met. Chem. Eng.*, 1912, X, 540.

<sup>5</sup> *J. Inst. Met.*, 1912, VII, 265.

<sup>6</sup> *Bull. Soc. d'Enc.*, 1896, I, 1310; "Contributions à l'étude des alliages," 1901, 109.

<sup>7</sup> *J. Soc. Chem. Ind.*, 1906, XXV, 616; *Electrochem. Met. Ind.*, 1905, III, 396.

<sup>8</sup> *Zt. anorg. Chem.*, 1907, LV, 412.

<sup>9</sup> *Rev. Mét.*, 1907, IV, 1077.

<sup>10</sup> *Internat. Zt. Metallographie*, 1913, III, 195.

<sup>11</sup> Lawrie, *Tr. A. I. M. E.*, 1909, XL, 604, believes that the figures 0.025 and 0.05 per cent. ought to be reversed.

<sup>12</sup> Roberts-Austen, *Second Report Alloys Research Committee*, 1893, p. 121.

<sup>13</sup> *Loc. cit.*

<sup>14</sup> Johnson, *J. Inst. Met.*, 1910, VIII, 570.

<sup>15</sup> Parravano, *Internat. Zt. Metallographie*, 1911, I, 75.

<sup>16</sup> Archbutt's Forging Tests, *J. Inst. Met.*, 1912, VII, 264.

<sup>17</sup> *Zt. anorg. Chem.*, 1908, LVII, 9; *Metallurgie*, 1908, V, 298; *Rev. Mét.*, 1908, V, 366.

terminals of the curve, where Cu forms a solid solution with from 2 to 3 per cent. Fe, and Fe the same with a small amount of Cu. The first solution is found in the incomplete diagram of Heycock and Neville<sup>1</sup> and shown in the photomicrograph of Stead;<sup>2</sup> the latter states that Cu with up to 2.73 per cent. Fe shows only a single micrographical constituent, and that Fe with as much as 8 per cent. Cu appears free from any copper-colored compound. Ruer-Fick<sup>3</sup> draw the limits of solid solutions at 3 per cent. Fe and 9 per cent. Cu. Pfeiffer,<sup>4</sup> on the other hand, considers that Fe and Cu form heterogeneous mixtures throughout the whole series of alloys. The evidence for solid solutions at the terminals appears convincing. Iron is always likely to be present in Cu; it makes it hard and brittle, but less so than does Pb; the red color of Cu changes gradually to gray with an increase of Fe.

**12. Manganese.**—Copper and manganese form alloys that are frequently called manganese-bronzes. Their constitution has been investigated by Wolgodin,<sup>5</sup> Schemtuny-Urasow-Rykowskow,<sup>6</sup> and Sahmen.<sup>7</sup> The curves of the last two investigators show a solid solution; the curve of Sahmen has an apparent minimum between 30 and 40 per cent. Mn. The alloys become harder as the percentage of Mn increases. With from 0 to 80 per cent. Cu, the alloys are gray; beyond this they become yellowish; and with 96 per cent. Cu, reddish. All the alloys are non-magnetic. An addition of from 2 to 3 per cent. Mn to Cu<sup>8</sup> increases the tensile strength and the elastic limit, but not materially the hardness. An alloy with 8 per cent. Mn is malleable and ductile; one with 12–15 per cent. Mn is brittle; such alloys ought to be free from Pb or Sb.

There exist cupro-ferro-manganese alloys prepared by the addition of ferro-manganese to Cu.<sup>9</sup>

**13. Nickel.**—The leading freezing-point curves published are those of Guertler-Tammann,<sup>10</sup> Kurnakow-Schemtuny,<sup>11</sup> and Tafel.<sup>12</sup> The two metals form solid solutions throughout. The alloys rich in Cu are not attracted by the magnet; those rich in Ni are. Nickel makes Cu pale red and hard; 0.3 per cent. Ni shows no effect, 2–3 per cent. greatly increases the hardness and raises the tensile strength. The presence of Sb increases the effects of Ni; hence in the

<sup>1</sup> *Philos. Trans. A.*, 1897, CLXIX, 189.

<sup>2</sup> *J. Iron Steel Inst.*, 1901, II, 108.

<sup>3</sup> *Ferrum*, 1913, XI, 39.

<sup>4</sup> *Metallurgie*, 1906, III, 281.

<sup>5</sup> *Rev. Mét.*, 1907, IV, 25.

<sup>6</sup> *Zt. anorg. Chem.*, 1908, LVII, 253; *Rev. Mét.*, 1908, V, 371.

<sup>7</sup> *Zt. anorg. Chem.*, 1908, LVII, 201; *Rev. Mét.*, 1908, V, 373.

<sup>8</sup> Lewis, *J. Soc. Chem. Ind.*, 1902, XXI, 842.

Guillet, *Étude industrielle des alliages*, Dunod-Pinat, Paris, 1906, p. 752.

Heussler, *Verh. Ver. Bef. Gewerbebl.*, 1903, LXXXII, 277; *Iron Age*, June 28, 1904, p. 18.

<sup>9</sup> Parravano, *Int. Zt. Metallographie*, 1913, IV, 171; *Metall-Erz*, 1913, X, 503; *J. Inst. Mét.*, 1913, IX, 213.

<sup>10</sup> *Zt. anorg. Chem.*, 1907, LII, 25; *Rev. Mét.*, 1908, V, 375.

<sup>11</sup> *Zt. anorg. Chem.*, 1907, LIV, 151; *Rev. Mét.*, 1908, V, 377.

<sup>12</sup> *Metallurgie*, 1908, V, 343, 375.

presence of from 2 to 3 per cent. Ni, the Sb ought to be absent. However, 0.3 Ni+Sb does not affect the malleability in cold-working. According to Stahl,<sup>1</sup> Mansfeld copper with one-tenth per cent. Ni has a tensile strength of 31,000–47,000 lb. per square inch; an elongation in 8 in. of 39.5–46.0 per cent.; and a reduction of area of 50.5–60.7 per cent. The Cu–Ni–Fe series of alloys has been investigated by Vogel.<sup>2</sup>

**14. Cobalt.**—The Cu–Co alloys are at present of no industrial importance. Freezing-point curves have been traced by Konstantinow<sup>3</sup> and Sahmen.<sup>4</sup>

**15. Arsenic.**—Passing over the earlier work of Hiorns,<sup>5</sup> there exist two freezing-point curves by Friedrich<sup>6</sup> and by Bengough-Hill.<sup>7</sup> The revised curve of Friedrich, Fig. 13, shows the following: Cu forms with As a solid solution reaching with 684° C. a maximum in

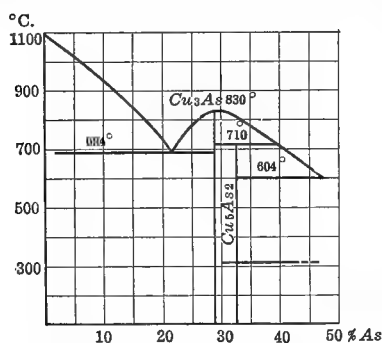


FIG. 13.—Alloy-series Cu-As.

4 per cent. As at the terminus of the eutectic line; the eutectic with 78.5 per cent. Cu is made up of the solid solution of Cu with 4 per cent. As and the compound  $\text{Cu}_3\text{As}$ ; the summit, 830° C., represents  $\text{Cu}_3\text{As}$  with 71.8 per cent. Cu. A hidden chemical compound,  $\text{Cu}_5\text{As}_2$  (67.9 per cent. Cu), is formed at 710° C. Nothing is definitely settled regarding the eutectic line at 604° C., and the transformation line at 307° C. Bengough-Hill confirm the existence of the compounds

$\text{Cu}_3\text{As}_2$  and  $\text{Cu}_5\text{As}_2$ , but believe that there exists a series of solid solutions between these compounds.

The mechanical properties of Cu are not harmed by 0.5 per cent. As; with 0.8 per cent. As copper can be drawn into the finest wire; 1 per cent. As begins to cause red-shortness.<sup>8</sup> The amount of O present in Cu has a decided influence upon the permissible quantity of As, as As does not reduce  $\text{Cu}_2\text{O}$ ;<sup>9</sup> thus 0.4 per cent.  $\text{Cu}_2\text{O} \cdot x \text{As}_2\text{O}_5$  has no effect whatever upon the mechanical properties of Cu, while more than 0.4 per cent. causes cold-shortness. Stahl<sup>10</sup> states that Cu with 0.30–0.35 per cent. As has a tensile strength of 28,000–29,200 lb. per square inch; an elongation of 33–44 per cent. with a reduction of area of 47–62

<sup>1</sup> *Op. cit.*, 1909, VI, 610, 1910, VII, 14; discussions by Heckman, *op. cit.*, 1910, VI, 760.

<sup>2</sup> *Zt. anorg. Chem.*, 1910, LXVII, 1.

<sup>3</sup> *Rev. Mét.*, 1907, IV, 983; *Min. Ind.*, 1907, XVI, 377.

<sup>4</sup> *Zt. anorg. Chem.*, 1908, LVII, 1; *Rev. Mét.*, 1908, V, 364.

<sup>5</sup> *Electrochem. and Met.*, 1903–04, III, 648, 734; *Electrochem. Ind.*, 1904, II, 170; *Min. Ind.*, 1903, XII, 124; *J. Inst. Met.*, 1910, III, 54.

<sup>6</sup> *Metallurgie*, 1905, II, 484; 1908, V, 529.

<sup>7</sup> *J. Inst. Met.*, 1910, III, 34.

<sup>8</sup> See Roberts-Austen, *Second Report, Alloys Research Committee*, 1893, p. 119.

<sup>9</sup> Jolibois-Thomas, *Rev. Mét.*, 1913, X, 1204.

<sup>10</sup> *Metallurgie*, 1909, VI, 611.

per cent. The following table of Lewis<sup>1</sup> shows the influence of As upon the tensile strength of Cu; other data are given by Bengough-Hill.<sup>2</sup> Lewis<sup>3</sup> states that Cu with from 1 to 1.37 per cent. As rolls very well; that the tensile strength is from 6,000 to 10,000 lb. higher than that of ordinary sheet copper; and that the elongation is not reduced. However, 0.6 per cent. As is generally considered the limit for good copper. Bengough-Hill found that Cu with less than 1 per cent. As was ruined when annealed in a reducing atmosphere above 650° C. The effects of As upon electric conductivity and absorption of gases has been discussed in § 4.

TABLE 6.—INFLUENCE OF ARSENIC UPON TENSILE STRENGTH OF COPPER

As, per cent.	Tensile strength, lb. per. sq. in.	Elongation, per cent.	Elastic limit, lb. per. sq. in.
0.00	26,800	25	14,000
0.24	33,840	27.5	20,500
0.53	36,760	29.5	19,020
0.75	36,620	21	17,820
0.94	36,040	25	18,020
1.37	37,660	28	20,180
1.80	35,660	20	23,040

**16. Antimony.**—The constitution of copper-antimony alloys has been investigated by Baikoff<sup>4</sup> and Hiorns.<sup>5</sup> Baikoff's curve is shown in Fig. 14. Starting with the Sb-end at 629° C., Sb is seen to form a solid solution  $\alpha$  with Cu reaching its maximum with 10 per cent. Cu;  $B$  (524° C., 25 per cent. Sb) is the eutectic point of the mixture of solid solution  $\alpha$  and chemical compound  $\text{Cu}_2\text{Sb}$ , the eutectic line extending to 51 per cent. Cu. This compound, which has a characteristic purple color, is formed at 584° C. by the grayish compound  $\text{Cu}_3\text{Sb}$  combining with Sb according to  $2 \text{Cu}_3\text{Sb} + \text{Sb} = 3 \text{Cu}_2\text{Sb}$ . The compound  $\text{Cu}_3\text{Sb}$  (61.5 per cent. Cu) solidifies at 681° C; between 681 and 584° C., the solid solution  $\beta$  of  $\text{Cu}_3\text{Sb}$  and Sb (51–53.5 per cent. Cu) separates, and is transformed at 584° C. in part into  $\text{Cu}_2\text{Sb}$  and  $\beta$ . Between 53.5 and 69 per cent. Cu the solid solution  $\beta$  separates unchanged. Between 69 and 96 per cent. Cu there

<sup>1</sup> *J. Soc. Chem. Ind.*, 1901, XX, 254.

<sup>2</sup> *J. Inst. Met.*, 1910, III, 37.

Johnson, *J. Inst. Met.*, 1910, IV, 163; *Met. Chem. Eng.*, 1910, VIII, 570; *J. Inst. Met.*, 1912, VIII, 192; 1913, X, 275.

Lewis, *Met. Chem. Eng.*, 1912, X, 540.

\*Greaves, *J. Inst. Met.*, 1912, VII, 218.

Archbutt, *op. cit.*, 1912, VII, 262.

Law, *op. cit.*, 1912, VIII, 222.

Baucke, *Internat. Zt. Metallographie*, 1913, III, 195.

<sup>3</sup> *Engineering*, 1903, LXXVI, 733; *J. Soc. Chem. Ind.*, 1903, XXII, 1351.

<sup>4</sup> *Bull. Soc. d'Encour.*, 1903, I, 626; *Rev. Mét. Extr.*, 1905, II, 433.

<sup>5</sup> *J. Soc. Chem. Ind.*, 1906, XXV, 616.

separates above  $630^{\circ}\text{C.}$  the solid solution of  $\text{Cu}_3\text{Sb}$  and  $\gamma$ , and a solid solution of Cu with 2.5 per cent. Sb; below  $630^{\circ}\text{C.}$  the former is transformed into  $\beta$  and  $\gamma$  solution; below  $407^{\circ}\text{C.}$  the last transformation takes place, leaving on the antimony side of the ordinate 61 per cent. Cu, the mixture of  $\text{Cu}_2\text{Sb}$  and  $\text{Cu}_3\text{Sb}$ , and on the copper side  $\gamma$  and  $\text{Cu}_3\text{Sb}$ .

The effect of Sb upon the mechanical properties of Cu is similar to that of As. Sb does not reduce  $\text{Cu}_2\text{O}$ .<sup>1</sup> The tensile strength is increased by Sb. Thus Hampe<sup>2</sup> showed that Cu with 0.26 per cent. Sb gave 73,800 lb., and with 0.529

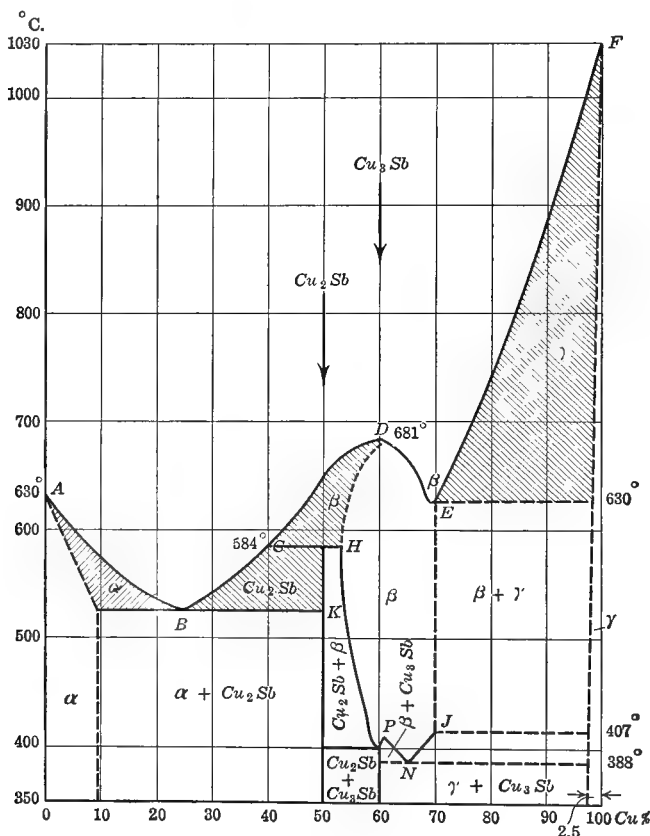


FIG. 14.—Alloy-series Cu-Sb.

per cent., 77,900 lb. per square inch.; the sample with 0.529 per cent. Sb could still be drawn to a fine wire; 1 per cent. Sb caused cold-shortness. The so-called copper-mica ( $6\text{Cu}_2\text{O} \cdot \text{Sb}_2\text{O}_5 + 8\text{NiO} \cdot \text{Sb}_2\text{O}_5$ , gold-colored to yellowish-green scales, formed in refining Cu containing both Sb and Ni, can be present to the extent of 0.726 per cent. and not interfere with malleability, but does affect ductility;

<sup>1</sup> Jolibois-Thomas, *Rev. Mét.*, 1913, X, 1264.

<sup>2</sup> *Chemiker Z.*, 1892, XVI, 726, *Second Report, Alloys Research Comm.*, 1893, p. 120.



1.44 per cent. of the salt makes Cu red-short. It is generally held that Cu should not contain over 0.05 per cent. Sb, as Cu with 0.1 per cent. Sb has been found to crack at the edges when it is rolled,<sup>1</sup> and cannot be bent without breaking. Other data are given by Greaves,<sup>2</sup> Archbutt,<sup>3</sup> Johnson,<sup>4</sup> and Law.<sup>5</sup>

**17. Sulphur.**<sup>6</sup>—Sulphur is present in Cu as  $\text{Cu}_2\text{S}$ . The freezing-point curve Cu- $\text{Cu}_2\text{S}$  of Heyn-Bauer,<sup>7</sup> shown in Fig. 15, resembles that of Pb-Cu. Starting with  $\text{Cu}_2\text{S}$ , its melting-point of  $1127^\circ\text{C}$ . is lowered by additions of Cu; when the liquid is cooled and reaches the branch  $1127$ – $1102^\circ\text{C}$ ., metallic Cu separates with a lowering of temperature until the point at  $1102^\circ\text{C}$ . has been reached; a further separation of Cu causes no fall in temperature until the composition has been changed into that of the left terminus of  $1102^\circ\text{C}$ ., when upon further separation of Cu there is a quick descent of the curve to the eutectic point, 3.8 per cent.  $\text{Cu}_2\text{S}$ ,  $1067^\circ\text{C}$ ., followed by a quick rise to the freezing point  $1084^\circ\text{C}$ . of Cu.

Hampe has shown that Cu with 0.25 per cent. S is still malleable, and that 0.5 per cent. S makes it cold-short, but not red-short. On the other hand, Lewes<sup>8</sup> found that Cu with 0.1 per cent. S cracked badly on rolling and bent badly; and that 0.5 per cent. Mn or Al counteracted the bad effect of S. Sperry<sup>9</sup> found that as little as 0.1 per cent. S caused blowholes; and that the Cu could be forged, but would not stand bending without cracking.

**18. Selenium and Tellurium.**<sup>10</sup>—These two elements are found in pig copper in very small quantities, 0.007 per cent. in Montana copper according to Keller;<sup>11</sup> and are removed by electrolytic refining process to such an extent that they rarely appear in market copper.

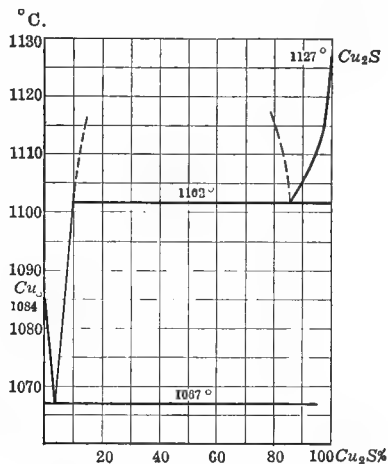


FIG. 15.—Alloy-series Cu- $\text{Cu}_2\text{S}$ .

<sup>1</sup> Lewis, *Engineering*, 1903, LXXVI, 753; *Am. Mfr.*, 1903, LXXIII, 903; *Met. Chem. Eng.*, 1912, x, 540.

<sup>2</sup> *J. Inst. Met.*, 1912, VII, 218.

<sup>3</sup> *Op. cit.*, 1912, VII, 262.

<sup>4</sup> *Op. cit.*, 1912, VIII, 192.

<sup>5</sup> *Op. cit.*, 1912, VIII, 222.

<sup>6</sup> Stahl, *Berg. Hüttenm. Z.*, 1890, XLIX, 99, 127.

Hinrichsen-Bauer, *Metallurgie*, 1907, IV, 315; *Oest. Zt. Berg. Hüttenw.*, 1907, LV, 473.

<sup>7</sup> *Metallurgie*, 1906, III, 76.

<sup>8</sup> *Engineering*, 1903, LXXVI, 73; *Am. Mfr.*, 1903, LXXIII, 904.

<sup>9</sup> *Brass World*, 1913, IX, 91.

<sup>10</sup> Microscopical tests: Heyn-Bauer, *Metallurgie*, 1906, III, 84.

Hinrichsen-Bauer, *op. cit.*, 1907, IV, 315; *Oest. Zt. Berg. Hüttenw.*, 1907, LV, 473.

<sup>11</sup> *Min. Ind.*, 1898, VII, 241.

Cuprous selenide,<sup>1</sup>  $\text{Cu}_2\text{Se}$ , melts at  $1113^\circ\text{C}$ . and forms with Cu an eutectic containing 2 to 3 per cent. Cu.

The constitution of Cu-Te alloys has been investigated by Chikashigé<sup>2</sup> and Pouchine.<sup>3</sup> There exist, according to the former, a gray  $\text{Cu}_2\text{Te}$ , a violet  $\text{Cu}_4\text{Te}_3$ , an eutectic  $\text{Te} + \text{Cu}_4\text{Te}_3$ , and several solid solutions; the latter found an additional compound  $\text{CuTe}$ . The metal was discovered by Egleston<sup>4</sup> in copper, which upon analysis showed 0.08 per cent. Te, and the copper was red-short.

**19. Silver.**—The first freezing-point curve, by Heycock-Neville<sup>5</sup>, determined the general eutectic character of the series of alloys; Friedrich and Leroux<sup>6</sup> of carried the work further, and Lepkowski<sup>7</sup> completed the curve fixing the extent the solid solutions at the terminals. The curve of the last, with atomic changed

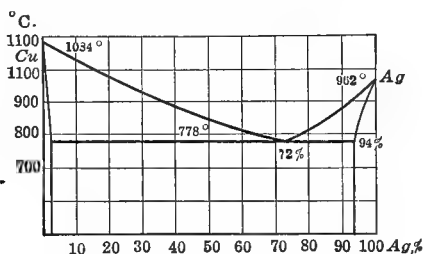


FIG. 16.—Alloy-series Cu-Ag.

into weight per cent., is given in Fig. 16. The eutectic point with 28 per cent. Cu lies at  $779^\circ\text{C}$ .; solid solutions are formed at the ends of the eutectic line, Cu holding 2 per cent. Ag and Ag 7 per cent. Cu. A knowledge of the structure is of importance for the correct sampling<sup>8</sup> of copper ingots that carry precious metal. The electric conductivity and hardness of Cu-Ag alloys have been studied by Kurnakow-Puschin-Senkowski,<sup>9</sup> and mechanical properties, hot and cold, by Johnson.<sup>10</sup>

**20. Lead and Silver.**—The investigation of Friedrich and Leroux<sup>11</sup> has shown that these metals form a ternary eutectic, with Cu 0.5 per cent., Ag 2.0 per cent.,

<sup>1</sup> Friedrich-Leroux, *Metallurgie*, 1908, v, 356.

<sup>2</sup> *Zt. anorg. Chem.*, 1907, LIV, 50; *Rev. Mét.*, 1908, v, 392.

<sup>3</sup> *Op. cit.*, 1907, IV, 929.

<sup>4</sup> *Tr. A. I. M. E.*, 1881-82, x, 493.

<sup>5</sup> *Phil. Trans. A.*, 1897, CLXXXIX, 25.

<sup>6</sup> *Metallurgie*, 1907, IV, 297-7.

<sup>7</sup> *Zt. anorg. Chem.*, 1908, XLIX, 289.

<sup>8</sup> Keller, *Tr. A. I. M. E.*, 1897, XVII, 106; 1911, XLII, 905; *Eng. Min. J.*, 1912, XCIII, 703, 729.

Ledoux, *School Mines Quart.*, 1897-98, XIX, 366.

Wraith, *Tr. A. I. M. E.*, 1910, XLI, 318.

Liddell, *Eng. Min. J.*, 1910, XC, 897, 953, 1095; 1911, XCII, 1173.

Smoot, *op. cit.*, 1912, XCIII, 1213.

<sup>9</sup> *Zt. anorg. Chem.*, 1910, LXVIII, 123.

*School Min. Quart.*, 1912, XXXIII, 405.

<sup>10</sup> *J. Inst. Met.*, 1910, IV, 163.

<sup>11</sup> *Metallurgie*, 1907, IV, 293.

Cu 97.5 per cent., which freezes at from 0.5 to 1° C. below the binary eutectic of Ag-Pb (300° C.).

**21. Gold.**—The first freezing-point curve was drawn by Roberts-Austen and Rose.<sup>1</sup> It has been supplemented by the work of Kurnakow and Schemtuny,<sup>2</sup> they show that the two metals form solid solutions throughout with a low point at 82 per cent. Au, as seen in Fig. 17. This disposes of the supposed existence of definite chemical compounds.<sup>3</sup> The ternary series Cu-Au-Ag has been studied by Jänecke.<sup>4</sup>

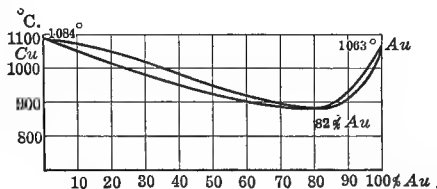


FIG. 17.—Alloy-series Cu-Au.

**22. Minor Metals.**—The following freezing-point curves are at present of little metallurgical importance: Cu-Ca,<sup>5</sup> Cu-Mg,<sup>6</sup> Cu-Cd,<sup>7</sup> Cu-Tl,<sup>8</sup> Cu-Pd,<sup>9</sup> Cu-Pt,<sup>10</sup> Cu-Va,<sup>11</sup> Cu-W,<sup>12</sup> Cu-Ti,<sup>13</sup> Cu-Cr,<sup>14</sup> Cu-Cd-Sb.<sup>15</sup>

<sup>1</sup> *Proc. Roy. Soc.*, 1901, LXVII, 105.

<sup>2</sup> *Zt. anorg. Chem.*, 1907, LIV, 159.

<sup>3</sup> Pearce, *Tr. A. I. M. E.*, 1884-85, XIII, 738.

<sup>4</sup> *Metallurgie*, 1911, VIII, 597; *J. Inst. Met.*, 1911, VI, 331.

<sup>5</sup> Donski, *Zt. anorg. Chem.*, 1908, LVII, 218; *Rev. Mét.*, 1908, V, 360.

Bensell, *Metall-Erz*, 1914, XI, 10, 46.

<sup>6</sup> Ursakow, *Chem. Centralblatt*, 1908, I, 1038; *Rev. Mét.*, 1908, V, 371.

Sahmen, *Zt. anorg. Chem.*, 1908, LVII, 26.

<sup>7</sup> Sahmen, *op. cit.*, 1906, XLIX, 301; *Rev. Mét.*, 1908, V, 362.

<sup>8</sup> Doerinkel, *Zt. anorg. Chem.*, 1906, XLVIII, 185; *Rev. Mét.*, 1908, V, 395.

<sup>9</sup> Ruer, *Zt. anorg. Chem.*, 1906, LI, 223; *Rev. Mét.*, 1908, V, 386.

<sup>10</sup> Doerinkel, *Zt. anorg. Chem.*, 1907, LIV, 335; *Rev. Mét.*, 1908, V, 388.

<sup>11</sup> Guillet, *Rev. Mét.*, 1906, III, 171; *Génie Civil*, 1905, XLVII, 147.

Norris, *J. Franklin Inst.*, 1911, CLXXI, 561.

<sup>12</sup> Guillet, *Rev. Mét.*, 1906, III, 171; *Génie Civil*, 1905, XLVII, 147.

<sup>13</sup> Rossi, *Electrochem. Met. Ind.*, 1908, VI, 257; 1909, VII, 88.

Bensell, *Metall-Erz*, 1914, XI, 10, 46.

<sup>14</sup> Guillet, *Rev. Mét.*, 1906, III, 171; *Génie Civil*, 1905, XLVII, 147.

Hindrichs, *Zt. anorg. Chem.*, 1908, XLIX, 414; *Electrochem. Met. Ind.*, 1909, VII, 34.

<sup>15</sup> Schleicher, *Internat. Zt. Metallographie*, 1912, III, 103.

## CHAPTER IV

### INDUSTRIAL ALLOYS

**23. Industrial Alloys in General.**<sup>1</sup>—Copper forms the basis of a large number of important alloys. As a rule they are more fusible and more fluid than copper. give sounder castings, are harder, less malleable and less corrodible.<sup>2</sup>

As regards the structure, it may be said that alloys in which copper forms an unsaturated solution with another metal show a high degree of toughness and malleability, while alloys in which copper forms an intermetallic compound or solid solutions with the compounds of the latter are usually hard and brittle.

The solubility of gases in copper alloys<sup>3</sup> is similar to that in copper.<sup>4</sup> Thus the solubility of SO<sub>2</sub> increases with the rise in temperature and is proportional to the square root of the gas pressure.

The mechanical properties of the alloys are greatly affected by a rise in temperature.<sup>5</sup> The behavior of copper has been illustrated in Fig. 4; examples of alloys are given in Figs. 25, 26, 36, 37, 38.

<sup>1</sup> Japing, E., "Kupfer und Messing," Hartleben, Leipsic, 1883.

Guettier, A., "Le fondeur en métaux," Bernard, Paris, 1890.

Wüst, F., "Handbuch der Metallgiesserei," Voigt, Weimar, 1897.

Thurston, R. H., "A Treatise on Brasses, Bronzes and other Alloys," Wiley, New York, 1900.

Guillet, L., "Les alliages métalliques," Dunod, Paris, 1906.

Brannet, W. T., "The Metallic Alloys," Baird, Philadelphia, 1908.

Krupp, A., "Die Legierungen," Hartleben, Leipsic, 1909.

Sexton, A. H., "Alloys, non-ferrous," Scientific Publ. Co., Manchester, 1909.

Law, E. F., "Alloys and their Industrial Applications," Griffin & Co., London, 1913.

Buchanan, J. F., "Practical Alloying," Penton Publ. Co., Cleveland, Ohio, 1910.

Kaiser, E. W., "Zusammensetzung der Gebräuchlichen Metallegierungen," Knapp, Halle, 1911-12.

Schott, E. A., "Die Metallgiesserei," Voigt, Leipsic, 1913.

Hiorns, A. H., "Mixed Metals and Metallic Alloys," Macmillan, London, 1913.

Buchner, G., "Die Metallfärbung," Krayn, Berlin, 1910.

Brown, W. N., "Dipping, Burnishing, Lacquering, etc.," Scott, Greenwood & Sons, London, 1912.

Gowland, "History," *J. Inst. Met.*, 1912, VII, 23.

<sup>2</sup> Diegel, *Verh. Verein. Beförd. Gewerb.*, 1899, LXXVIII, 313; 1903, LXXXII, 93, 119, 157.

Bengough and Bengough-Jones, *Reports of Corrosion Committee, J. Inst. Met.*, 1911, V, 28, 1913, X, 13.

<sup>3</sup> Sievert-Bergner, *Zt. phys. Chem.*, 1913, LXXXII, 257; *J. Inst. Met.*, 1913, IX, 231.

<sup>4</sup> See § 4.

<sup>5</sup> Gard, *Rev. Mét.*, 1909, IV, 1069.

Weidig, *Verh. Verein. Beförd. Gewerb.*, 1911, XC, 455, 525.

Johnson, *Met. Chem. Eng.*, 1911, IX, 399.

Bengough, *J. Inst. Met.*, 1912, VII, 123.

Huntington, *op. cit.*, 1912, VIII, 126.

Müller, *Metall-Erz*, 1913, I, 219.

In the preparation of alloys<sup>1</sup> the pouring temperature shows a decided influence upon the closeness of the grain and thereby upon the strength of the product.

The leading copper alloys are those with zinc, tin, aluminum, gold (§ 21), and silver (§ 19); of secondary importance are the alloys with phosphorus, silicon, and manganese, which are reviewed first.

The melting-points of the following common industrial alloys have been determined by Gillett-Brown.<sup>2</sup>

TABLE 6A.—MELTING-POINTS OF SOME COMMON INDUSTRIAL ALLOYS

Alloy	Composition desired				Composition by analysis				Melting-point (liquidus) ° C.
	Cu	Zn	Sn	Pb	Cu	Zn	Sn	Pb	
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	
Gun metal.....	88	2	10	.....	.....	.....	.....	.....	995
Leaded gun metal....	85½	2	9½	3	85.4	1.9	9.7	3.0	980
Red brass.....	85	5	5	5	.....	.....	.....	.....	970
Low-grade red brass..	82	10	3	5	81.5	10.4	3.1	5.0	980
Leaded bronze.....	80	.....	10	10	.....	.....	.....	.....	945
Bronze with zinc....	85	5	10	.....	84.6	5.0	10.4	.....	980
Half yellow; half red.	75	20	2	3	75.0	20.0	2.0	3.0	920
Cast yellow brass....	67	31	.....	2	66.9	30.8	.....	2.3	895
Naval brass.....	61½	37	1½	.....	61.7	36.9	1.4	.....	855
	Cu	Zn	Sn	Fe	Al	?		Mn	
Manganese bronze...	56	41	0.9	1.5	0.45	.....	.....	0.15	870

**24. Phosphor-copper.**—The constitution of these alloys is shown by the curve of Heyn and Bauer,<sup>3</sup> Fig. 18. This curve shows an eutectic with 8.27 per cent. P melting at 707° C.; the chemical compound  $\text{Cu}_3\text{P}$  with 14.1 per cent. P freezing at 1100° C.; one solid solution of Cu with a maximum of 0.175 per cent. P, and another of  $\text{Cu}_3\text{P}$  with a probable second chemical compound  $\text{Cu}_5\text{P}_2$ .<sup>4</sup>

Alloys are prepared in two ways; either by plunging stick-P, held in an inverted cup,<sup>5</sup> into Cu, melted in a crucible, and keeping it submerged until it has been taken up, or by causing

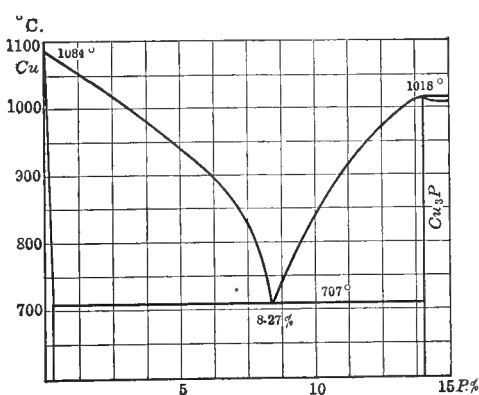


FIG. 18.—Alloy-series Cu-P.

<sup>1</sup> Gillett, *Eighth Internat. Congress Appl. Chem.*, New York, 1912, II, 105.

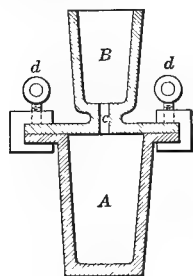
<sup>2</sup> Bureau Mines, Techn. Paper 60., 1913.

<sup>3</sup> *Zt. anorg. Chem.*, 1907, LII, 131; *Metallurgie*, 1907, IV, 242, 257; *Rev. Mét.*, 1908, V, 377.

<sup>4</sup> Huntington and Desch, *Tr. Faraday Soc.*, 1908-09, IV, 51.

<sup>5</sup> Wickhorst, *Iron Age*, March 25, 1897, p. 2.

fused Cu to combine with P-vapor. The apparatus for the second method, shown in Fig. 19,<sup>1</sup> consists of the crucible *A* clamped to the funnel *B* with discharge-opening *c*. Phosphorus is placed in *A* and molten copper poured into *B*. The phosphorus in *A* is vaporized and forced to pass through the copper as it flows through *c*. As an alloy containing over 14.1 per cent. P gives off P upon heating, alloys with over 14–15 per cent. P cannot be produced by fusion. Heyn states that alloys with as much as 20 per cent.



Scale of  $\frac{1}{16}$

FIG. 19.—Apparatus for preparing phosphor-copper.

P can be produced by mixing Cu-filings and red P in crucibles, connected in series wash-bottle fashion, and heating one at a time to 300–400° C., but not over 700° C., when the vapors from the crucible that is being heated will be condensed by the others.

The commercial alloy contains from 9 to 15 per cent. P; it is steel gray, so hard that it can be filed only with difficulty, fine-grained and brittle.

Small additions of P make Cu hard; Cu with 0.05–0.10 per cent. P and not over 0.04 per cent. O is still easily rolled.<sup>2</sup> Hiorns<sup>3</sup> found that Cu with 0.5 per cent. P rolled well giving smooth edges; and Munker<sup>4</sup> maintains that pure copper with 1 per cent. P may be rolled hot or cold, but that the ductility is much reduced by 0.2 per cent. P. The constitutional diagram shows that with over 0.175 per cent. P the eutectic, containing hard brittle  $\text{Cu}_3\text{P}$ , separates.

USES OF PHOSPHORUS-COPPER ALLOYS.—The principal use of the commercial alloy is in the manufacture of the so-called phosphorbronze; it is added to Cu that is to be rolled, as the metal appears to work more evenly owing to the deoxidation of the  $\text{Cu}_2\text{O}$  present. It has been suggested for use in the refining of coarse copper in order to assist in the removal of O according to  $6\text{Cu}_2\text{O} + 2\text{P} = 10\text{Cu} + 2\text{CuO} \cdot \text{P}_2\text{O}_5$ . Alloys of Cu and Mn<sup>5</sup> have been used for this purpose. Stahl<sup>6</sup> shows that the addition of such alloys increases the specific gravity of commercial Cu by reducing the  $\text{Cu}_2\text{O}$  that is present and by diminishing the absorbing power for gas.

**25. Silicon-copper.**<sup>7</sup>—The freezing-point curve of Rudolfi<sup>8</sup> (Fig. 20)

<sup>1</sup> Hiorns, A. H., "Mixed Metals," Macmillan, New York, 1913, p. 219.

<sup>2</sup> Lewis, *loc. cit.*; *Met. Chem. Eng.*, 1912, x, 540.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1906, xxv, 622.

<sup>4</sup> *Metallurgie*, 1912, ix, 185; *J. Inst. Met.*, 1912, vii, 272.

<sup>5</sup> Rössler, *Berg. Hüttenm. Z.*, 1878, xxxvii, 370; *Zt. Berg. Hütten. Sal. Wes. i. Pr.*, 1879, xxvii, 14; *Eng. Min. J.*, 1880, xxix, 317.

Lewitzky, *Berg. Hüttenm. Z.*, 1880, xxxix, 64; *Rev. Un. Min.*, 1879, vi, 24.

<sup>6</sup> *Berg. Hüttenm. Z.*, 1901, lx, 78.

<sup>7</sup> Phillips, *Metallurgie*, 1907, iv, 587, 613; *Electrochem. Met. Ind.*, 1907, v, 468.

Baraduc-Muller, *Rev. Mét.*, 1910, vii, 711.

Frilley, *op. cit.*, 1911, viii, 511.

<sup>8</sup> *Zt. anorg. Chem.*, 1907, liii, 216; *Metallurgie*, 1907, iv, 851; *Rev. Mét.*, 1908, v, 390.

replaces for the present the older approximations<sup>1</sup> of the constitution of copper-silicon alloys, although objections have been made to some of its features.<sup>2</sup> Starting at the Cu-end of the curve, it is seen that Cu forms with Si a solid solution reaching 4.5 per cent. Si, next comes a hidden chemical compound  $\text{Cu}_{19}\text{Si}_4$  (8.59 per cent. Si) which forms with the second chemical compound  $\text{Cu}_3\text{Si}$  (12.95 per cent. Si, (melting at  $862^\circ\text{C.}$ ) the first eutectic (8.3 per cent. Si, freezing-point  $829^\circ\text{C.}$ ); the second eutectic of  $\text{Cu}_3\text{Si} + \text{Si}$ , with about 18 per cent. Si, freezes at  $710^\circ\text{C.}$  Photomicrographs have been published by Arnold-Jefferson<sup>3</sup> and Albro.<sup>4</sup>

Copper-silicon alloys have been prepared in various ways.<sup>5</sup> Electrothermic methods have probably replaced the earlier modes of operating; and in these the electric fusion of a mixture of Cu, sand, and C in a resistance furnace has given place to the simple fusion of Si and Cu, since metallic Si is produced on a large scale and is sold at a reasonable price. The Cowles Electric Smelting and Aluminum Co., Lockport, N. Y., produces pure silicon-copper with 20-30 per cent. Si, sold in ingots weighing about 14 lb.; details of the method of working have not been made public.

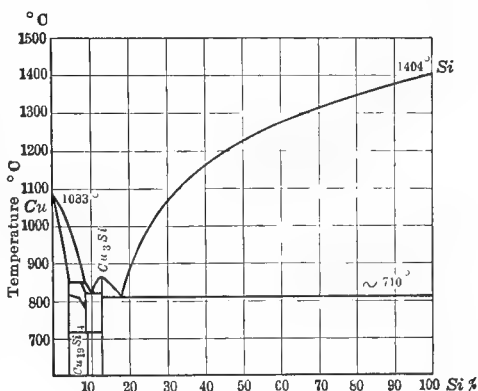


FIG. 20.—Alloy-series Cu-Si.

Copper-silicon alloys are brittle, and the more so the higher the Si-content. The 20-30 per cent. alloy is easily broken into glassy splinters by a tap with a hammer; a fresh surface is silvery and assumes a reddish tint when exposed to the air.

According to Hampe<sup>6</sup> an addition of Si to Cu increases the hardness and at the same time assists in the production of sound castings; 3.472 per cent. Si does not reduce the tensile strength and malleability of copper; 6 per cent.

<sup>1</sup> DeChalmot, *Am. Chem. J.*, 1897, XIX, 118, 871; 1896, XVIII, 95; 1898, XX, 437.

Lebeau, *Sixth Int. Cong. Appl. Chem.*, 1906, II, 411.

Vigouroux, *Compt. rend.*, 1896, CXXII, 318; 1905, CXLI, 890; 1906, CXLII, 87; 1907, CXLIV,

1214.

<sup>2</sup> Bornemann, *Metallurgie*, 1907, IV, 852.

Guertler, *Phys. Chem. Centralblatt*, 1907, IV, 576.

Rudolfi, *op. cit.*, 1908, V, 223.

Portevin, *Rev. Mét.*, 1908, V, 391.

<sup>3</sup> *Eng. Min. J.*, 1896, LXI, 353.

<sup>4</sup> *Electrochem. Met. Ind.*, 1905, III, 461.

<sup>5</sup> Maberry, *Am. Assoc. Adv. Sc.*, 1886, XXXIV, 136.

Hunt, *Tr. A. I. M. E.*, 1885-86, XIV, 492.

Steinhardt, *Eng. Min. J.*, 1899, LXVII, 710.

Kroupa, *Oest. Zt. Berg. Hüttenw.*, 1903, LI, 285.

<sup>6</sup> *Chem. Z.*, 1892, XVI, 726; *Berg. Hüttenm. Z.*, 1892, LI, 321.

makes it brittle; Cu with 8 per cent. Si can be pulverized; with 11.7 per cent. Si it is as brittle as glass. Rudolf<sup>1</sup> states that Cu with 5 per cent. Si is readily drawn into wire. According to Davis<sup>2</sup> the addition of 0.1 per cent. Si to melted Cu increases the fluidity and gives castings that are clean and free from blow-holes, which is due probably<sup>3</sup> to the reduction of  $\text{Cu}_2\text{O}$ . The cast alloy 97 Cu and 3 Si has a tensile strength of 55,000 lb. per square inch and from 50 to 60 per cent. ductility; the cast alloy 95 Cu and 5 Si has 75,000 lb. tensile strength and 80 per cent. ductility; over 5 per cent. Si makes Cu brittle. An analysis of Si-Cu spring-wire<sup>4</sup> gave Cu 97.59, Si 2.31, Fe 0.10.

**26. Brass (Cu-Zn) in General.**—The constitution of brass has been a subject of study since the days of Storer.<sup>5</sup> The leading freezing-point curves are

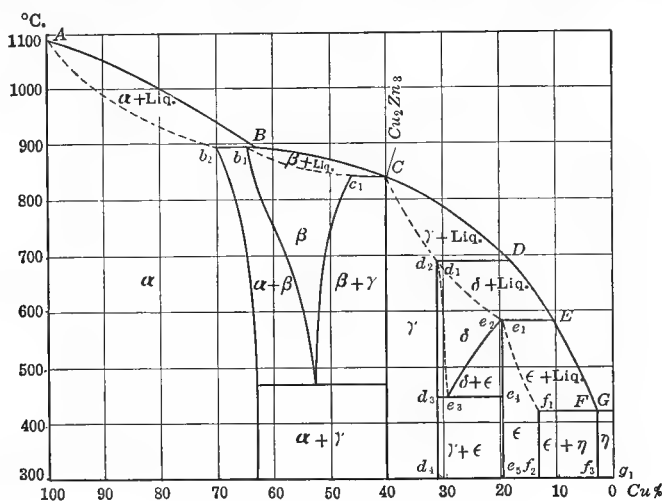


FIG. 21.—Alloy-series Cu-Zn brass.

those of Roberts-Austen,<sup>6</sup> Sheperd,<sup>7</sup> Sackur,<sup>8</sup> Tafel,<sup>9</sup> and Carpenter-Edwards.<sup>10</sup> The curves of Sheperd and Tafel resemble one another. Sheperd holds that there are no chemical compounds; Tafel that the compound  $\text{Cu}_2\text{Zn}_3$  (Cu 39.33, Zn 60.67, melting-point,  $830^\circ\text{C}$ .) is established and that possibly there is a second compound  $\text{CuZn}$  (Cu 49.3, Zn 50.7).<sup>11</sup> Carpenter-Edwards have added

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Aluminum World*, 1896, III, 241.

<sup>3</sup> *Vickers, Foundry*, 1908, XXXII, 1.

<sup>4</sup> *Brass World*, 1905, I, 413.

<sup>5</sup> *Mem. Am. Academy*, 1860, VIII, 27.

<sup>6</sup> *Fourth Rep. Alloys Research Comm.*, 1897, p. 31.

<sup>7</sup> *J. phys. chem.*, 1904, VIII, 421; *Metallurgie*, 1904, I, 462.

<sup>8</sup> *Ber. deutsch. chem. Ges.*, 1905, XXXVIII, 2186.

<sup>9</sup> *Metallurgie*, 1908, V, 349, 375, 413 (incl. bibliography pp. 343, 349).

<sup>10</sup> *J. Inst. Met.*, 1911, V, 127, 1912, VIII, 51, 59.

<sup>11</sup> *Guertler, Zt. anorg. Chem.*, 1906, LI, 429.

Hudson, *J. Soc. Chem. Ind.*, 1906, XXV, 503.

Bengough-Hudson, *op. cit.*, 1908, XXVII, 43, 654.



to the curves of Sheperd and Tafel a transformation point at  $470^{\circ}\text{C.}$ , below which the constituent  $\beta$  splits into  $\alpha + \gamma$ . The diagram of Sheperd-Tafel and Carpenter-Edwards is given in Fig. 21. It shows 6 constituents, the characteristics of which are assembled in Table 7.

TABLE 7.—CHARACTERISTICS OF COMPONENTS OF BRASS  
(Sheperd)

Component <sup>1</sup>	Color	Color of fracture
$\alpha$	Clear yellow to copper red . . .	
$\alpha + \beta$	Red changing to full yellow . . .	Yellow.
$\beta + \alpha$	Reddish yellow with a yellowish cast.	Yellowish red.
$\alpha + \gamma$	Light bluish gray	
$\beta$	Reddish yellow . . . . .	Yellowish red.
$\beta + \gamma$	Reddish yellow . . . . .	Yellowish red.
$\gamma + \beta$	Yellowish red . . . . .	Silvery with pinkish tinge.
$\gamma$	Silvery . . . . .	Silvery, very brilliant.
$\gamma + \epsilon + \delta$	Silvery gray to bluish gray . . .	Silvery gray, becoming duller.
$\epsilon$	Bluish gray . . . . .	Bluish gray.
$\epsilon + \eta$	Bluish gray, becoming lighter . .	Zinc color.
$\eta$	Zinc color . . . . .	Zinc color.

Alloys consisting of the solid solution  $\alpha$ , which has a range of from 100 to 64 per cent. Cu, can show no variety of structure. Figs. 22 and 23 are photomicrographs of common brass, 66.6 per cent. Cu, cast and annealed. The



FIG. 22.—Common brass, cast.



FIG. 23.—Common brass, annealed.

dendritic structure of the  $\alpha$ -crystals is due to the formation of copper-rich centers surrounded by zinc-rich borders, and to the attack on the borders by etching. The annealed specimen, in which equilibrium has been established between Cu and Zn, shows large polyhedral forms pitted irregularly by etching.

Alloys consisting of  $\alpha$ -crystals are malleable and ductile. Alloys with a composition lying between 64 and 54 per cent. Cu are likely to be brittle if cooled

<sup>1</sup> Constituents  $\alpha$  and  $\beta$  are malleable and ductile;  $\gamma$ ,  $\delta$ ,  $\epsilon$  and  $\eta$  are increasingly brittle.

slowly to below  $470^{\circ}\text{C.}$ , because of the presence of the constituent  $\gamma$ ; if chilled above  $470^{\circ}$  they will be tough, as they are made up of the components  $\alpha + \beta$ .

Murray<sup>1</sup> furnishes photomicrographs of the crystal forms  $\alpha - \eta$ ; and Charpy,<sup>2</sup> 48 illustrations of different industrial brasses. The leading mechanical properties<sup>3</sup> are shown in Fig. 24. The tensile strength is seen to grow with increase of zinc until it reaches a maximum with about 56 per cent. Cu (conglomerate  $\alpha$  and  $\beta$ , chilled above  $470^{\circ}\text{C.}$ ), and then to fall quickly (appearance of  $\gamma$  constituent); the elongation reaches its maximum earlier at about 70 per cent. Cu (limiting concentration of  $\alpha$ ); the compressive strength attains the largest

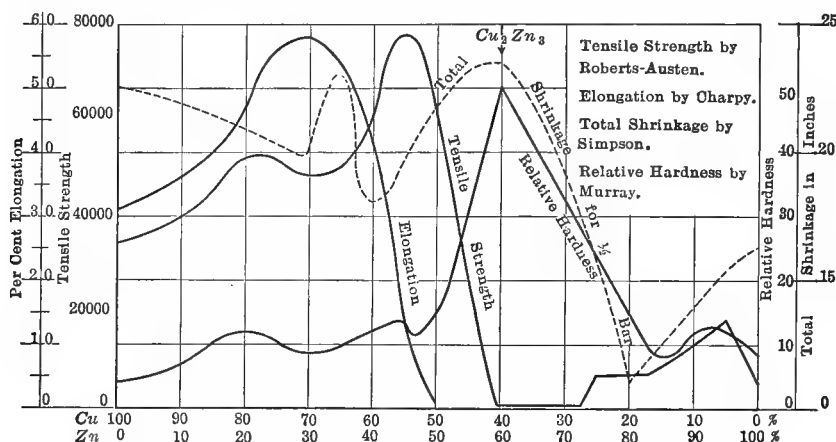


FIG. 24.—Mechanical properties of brass at ordinary temperature.

figure with 50 per cent. Cu. The total shrinkage<sup>4</sup> shows the largest maximum at 40 per cent. Cu; the same is the case with the hardness; and these two phenomena coincide with Tafel's chemical compound  $\text{Cu}_2\text{Zn}_3$ .

A table of the mechanical properties of a series of analyzed brasses, cast and annealed, was presented by Guillet and Revillon<sup>5</sup> at the London International Congress of 1909.

At elevated temperature the mechanical properties show other values than those given in Fig. 24 for ordinary temperature.<sup>6</sup>

<sup>1</sup> *J. Instit. Met.*, 1909, II, 1.

<sup>2</sup> "Contributions à l'étude des alliages," Paris, 1901, pp. 1-62.

<sup>3</sup> *J. phys. chem.*, 1913, XVII, 1; *J. Inst. Met.*, 1913, IX, 216; see also Bancroft-Lohr-Wilder, VIII, *Internat. Congr. Appl. Chem.*, 1912, II, 8.

<sup>4</sup> Turner-Murray, *J. Instit. Met.*, 1909, II, 98.

Wüst, *Metallurgie*, 1909, VI, 709; *Iron Age*, 1910, LXXXV, 790.

Chamberlain, *J. Inst. Met.*, 1913, X, 193.

<sup>5</sup> *Rev. Mét.*, 1909, VI, 1251.

<sup>6</sup> Bengough-Hudson, *J. Inst. Met.*, 1910, IV, 92.

Johnson, *Met. Chem. Eng.*, 1911, IX, 399.

Bengough, *J. Inst. Met.*, 1912, VII, 123.

Huntington, *op. cit.*, 1912, VIII, 126.

Guillet, "Wire-drawing," *Rev. Mét.*, 1913, X, 769.

The mechanical changes which two brasses,  $\frac{90}{10}$  and  $\frac{67}{33}$ , with  $\alpha$  and  $\alpha+\beta$  as components, undergo with increasing temperatures are shown in Figs. 25 and 26 by Grard.<sup>1</sup> Annealed brass has been hardened by mechanical treatment and then tested at temperatures ranging from zero to 900° C. The curves in Fig. 25, show for  $\frac{90}{10}$  brass that decided changes in the three mechanical properties given take place between 200 and 300° C., and that the same is the case with

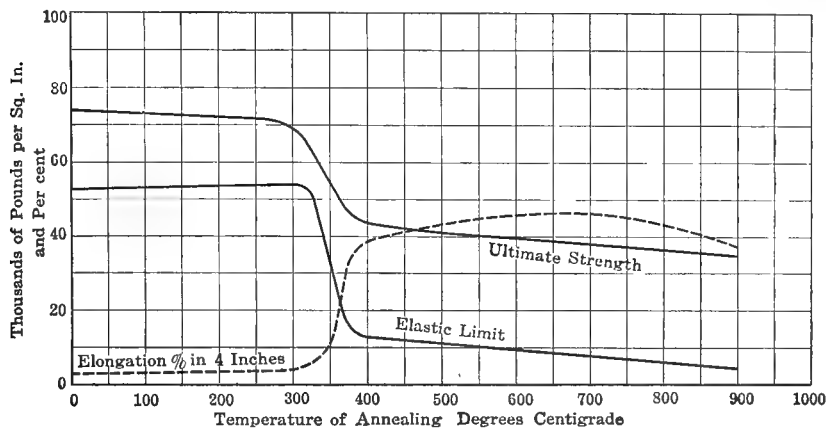


FIG. 25.—Mechanical properties of  $\frac{90}{10}$  brass at varying temperatures.

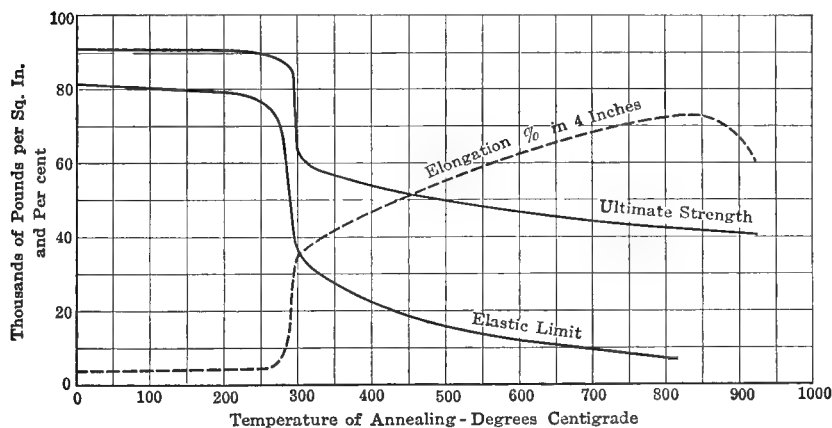


FIG. 26.—Mechanical properties of  $\frac{67}{33}$  brass at varying temperatures.

$\frac{67}{33}$  brass (Fig. 26) between 200 and 300° C. Additional data are furnished by Guillet.<sup>2</sup> The effects of annealing upon the structure have been studied by Portevin<sup>3</sup> and Robin.<sup>4</sup> When heated *in vacuo*,<sup>5</sup> the Zn is volatilized at a low temperature.

<sup>1</sup> *Rev. Mét.*, 1909, VI, 1069; *Metallurgie*, 1910, VII, 651; *Proc. Internat. Congress Testing Materials*, New York, 1912.

<sup>2</sup> *Rev. Mét.*, 1913, X, 671.

<sup>3</sup> *Op. cit.*, 1913, X, 677.

<sup>4</sup> *Op. cit.*, 1913, X, 764.

<sup>5</sup> Turner, *J. Inst. Met.*, 1912, VII, 105.

The electric conductivity of brass has been studied by Pushin and Rjaschsky.<sup>1</sup>

Upon heating in air, alloys with over 63 per cent. Cu show iridescent colors. The behavior, with acids, of alloys with < 50 per cent. Zn is similar to that of Cu; alloys with > 50 per cent. Zn are readily dissolved in acids which attack Zn but not Cu. The product of electrolytic corrosion<sup>2</sup> of brasses with > 50 per cent. Zn is practically Zn; with < 50 per cent. Zn it has the same composition as the alloy; or  $\alpha$ ,  $\alpha+\beta$ , and  $\beta$  brasses yield products of the same composition as the brasses;  $\gamma$  crystals diminish the corrosion;  $\gamma+\epsilon$ ,  $\epsilon$  and  $\eta$  brasses yield as product pure Zn. The fact that most industrial brasses lie within the range of  $\alpha$  or the conglomerate  $\alpha+\beta$ , makes them resistant to corrosion.<sup>3</sup> Brasses are likely to occlude gases<sup>4</sup> such as CO<sub>2</sub>, CO, and H.<sup>5</sup> In the manufacture<sup>6</sup> of brass the purity of the metals,<sup>7</sup> the apparatus used, and the temperature and time given to fusion and pouring, all have an influence upon the physical properties of the alloy. The O in Cu may have a harmful influence<sup>8</sup> in that it oxidizes Zn and causes infusible salamanders to form in the crucible. The presence of 0.01 per cent. O=0.09 per cent. Cu<sub>2</sub>O is harmless; good sheet brass has been rolled with copper containing 0.55 per cent. O=4.91 per cent. Cu<sub>2</sub>O, although the figure is excessive. According to Sperry as little as 0.02 per cent. Sb<sup>9</sup> or 0.02 per cent. Bi,<sup>10</sup> or 0.06 per cent. Te<sup>11</sup> makes common brass (60 Cu, 40 Zn) brittle so that it cannot be rolled without showing cracks; 0.8–0.9 per cent. Pb<sup>12</sup> causes no harm, but with 1 per cent. Pb trouble arises. An addition of 1.5–2 per cent. Pb<sup>13</sup> makes (screw or clock) brass sufficiently brittle to cut well with short chips. Similarly As, to the extent of 0.02 per cent.,<sup>14</sup> begins to affect the malleability; 1 per cent. Cd<sup>15</sup> appears to have no harmful influence except that

<sup>1</sup> *Zt. anorg. Chem.*, 1913, LXXXII, 50.

*J. Inst. Met.*, 1913, X, 420.

<sup>2</sup> Lincoln-Klein-Howe, *J. Phys. Chem.*, 1907, XI, 501.

Brühl, *J. Inst. Met.*, 1911, VI, 279.

<sup>3</sup> Diegel, *Stahl u. Eisen*, 1899, XIX, 170, 224.

Jones, *Met. Ind.*, 1905, III, 171.

Sexton, *Eng. Mag.*, 1905, XXX, 211.

Desch-Whyte, *J. Inst. Met.*, 1913, X, 314.

<sup>4</sup> Guillemin-Delachanal, *Rev. Mét.*, 1911, VIII, 1.

<sup>5</sup> Lewis, *Proc. Chem. Soc.*, 1912, XXVIII, 290; *J. Inst. Met.*, 1913, IX, 217.

<sup>6</sup> Brass Foundries: *Foundry*, 1902, XX, 142; 1903, XXIII, 169; 1906, XXVIII, 131; 1907, XXXI, 176, 285; *Met. Ind.*, 1908, VI, 341; *Iron Age*, 1912, LXXXIX, 1257; *Met. Ind.*, 1913, XI, 155.

<sup>7</sup> Carpenter, *J. Inst. Met.*, 1912, VIII, 59.

<sup>8</sup> Sperry, *Tr. A. I. M. E.*, 1900, XXX, 937.

Jolibois-Thomas, *Rev. Mét.*, 1913, X, 1264.

<sup>9</sup> *Tr. A. I. M. E.*, 1898, XXVIII, 176; *Brass World*, 1907, III, 297.

<sup>10</sup> Sperry, *Tr. A. I. M. E.*, 1898, XXVIII, 427.

Carpenter, *J. Inst. Met.*, 1912, VIII, 60.

<sup>11</sup> *Tr. A. I. M. E.*, 1903, XXXIII, 682.

<sup>12</sup> Guillet, *Rev. Mét.*, 1906, III, 273.

Johnson, *J. Inst. Met.*, 1912, VII, 201.

Carpenter, *op. cit.*, 1912, VIII, 63.

<sup>13</sup> Sperry, *Tr. A. I. M. E.*, 1897, XXVII, 485.

<sup>14</sup> Sperry, *Brass World*, 1906, II, 163.

<sup>15</sup> *Op. cit.*, 1907, III, 1211.

it hardens the alloy. S<sup>1</sup> makes brass pasty and is thus a cause of dirty castings; such pasty brass showed 0.69 per cent. S. Brass with 0.03 per cent. S rolls as well as common brass; it is not made red-short by S as is the case with Cu.

The effects of various impurities upon the constitution of brasses, especially upon the structure of the  $\beta$ -constituent, have been investigated by Carpenter.<sup>2</sup>

**MANUFACTURE OF BRASS.**—Brass is produced<sup>3</sup> by melting together Cu and Zn in a crucible furnace<sup>4</sup> which is usually fired with anthracite, coal or coke, sometimes with liquid, but rarely with gaseous fuel.<sup>5</sup> Electric induction furnaces are being advocated.<sup>6</sup> Oil- or gas-fired reverberatory furnaces are employed for melting ingot brass or bundled scrap and borings<sup>7</sup> after the iron has been removed by a magnet or the raw material first purified by washing.<sup>8</sup> Experiments have been made to produce brass from ZnS and Cu.<sup>9</sup>

In a crucible furnace the warmed Cu is charged first, melted under a 1-in. charcoal cover and kept just above its freezing-point. Then the necessary Zn, previously warmed, is added in several portions in order to prevent chilling of charge (the heating-up of which would cause much loss in Zn); the whole thoroughly stirred; brought quickly to the right temperature (100–200° C. above the melting-point; overheating causes oxidation, Zn begins to burn); skimmed or not; and poured into a suitable mold (sand, cast-iron, or bronze) to furnish an ingot to be sold or a plate to be rolled. In either case the alloy is chilled by spraying with water. Brass shrinks about  $\frac{3}{8}$  in. per foot, hence the cores are made soft.<sup>10</sup> Fluxes,<sup>11</sup> such as borax, are little used; sometimes salt<sup>12</sup> is added as a wash, although it assists the volatilization of Zn, and a deoxidizer<sup>13</sup> such as 0.0x per cent. Mg. An ordinary charge weighs from 50 to 200 lb.; 100 lb. is melted in about two hours; the loss in Zn may reach 6 per cent.<sup>14</sup> and has to be taken into account in making up the mixtures;<sup>15</sup> 1 lb. coke will melt about 2 lb. alloy; 1 man will operate 4 to 6 furnaces. The manufacture by electro-deposition is confined to plating.<sup>16</sup>

<sup>1</sup> Sperry, *op. cit.*, 1906, II, 307.

<sup>2</sup> *J. Inst. Met.*, 1912, VIII, 59.

<sup>3</sup> *Stahl u. Eisen*, 1913, XXXIII, 522.

<sup>4</sup> Horner, *Foundry*, 1913, XLI, 113, 119.

<sup>5</sup> Krom, "Development of Melting Furnaces," *Met. Ind.*, 1909, VII, 287, 324, 358, 404, 436; 1910, VIII, 80.

<sup>6</sup> Clamer-Hering, *Met. Chem. Eng.*, 1912, X, 702; *Foundry*, 1912, XL, 483; *Brass World*, 1912, VIII, 35.

Hansen, *Met. Chem. Eng.*, 1912, X, 703.

<sup>7</sup> *Brass World*, 1910, VI, 345; *op. cit.*, 1912, VIII, 421.

<sup>8</sup> Wittich, *Eng. Min. J.*, 1912, XCV, 853.

<sup>9</sup> Bense, *Metallurgie*, 1912, IX, 523.

<sup>10</sup> Chamberlain, Volume changes, *J. Inst. Met.*, 1913, X, 193.

<sup>11</sup> Krom, *Met. Ind.*, 1910, VIII, 203.

<sup>12</sup> Sperry, *Brass World*, 1912, VIII, 307.

<sup>13</sup> West, O in Cu and brass, *J. Inst. Met.*, 1913, X, 371.

<sup>14</sup> Bassett, *J. Ind. Eng. Chem.*, 1912, IV, 164.

<sup>15</sup> Sperry, Mixtures, *Brass World*, 1912, VIII, 41, 83, 121, 167, 204, 239, 285, 317.

Burkey, "Treatment of Brass Scrap," *Eng. Min. J.*, 1913, XCVI, 486.

<sup>16</sup> De Kay Thompson, *Met. Chem. Eng.*, 1912, X, 458.

Industrial brasses may be classed as regular and special; the former represent the binary alloys, the latter the Cu-Zn alloy with additional metals to furnish special properties.

**27. Regular Brass.**—There is a great variety in the regular brasses to meet the numerous requirements of the arts. The leading brasses are given in Table 8. The usual range of composition lies between 90 and 35 per cent. Cu; the most important alloys are those containing from 70 to 55 per cent. Cu. Alloys with more than 64 per cent. Cu are composed solely of  $\alpha$ -solution, while those between 64 and 55 per cent. Cu are made up of  $\alpha$  and  $\beta$  when quenched above  $470^{\circ}$ ; of  $\alpha + \gamma$  when cooled very slowly;  $\alpha$ -alloys are rolled or drawn<sup>1</sup> cold;  $\alpha - \beta$  ( $\alpha - \gamma$ ) alloys have to be rolled hot.



FIG. 27.—Rolled common brass which worked well.



FIG. 28.—Rolled common brass which worked unsatisfactorily.

In Table 8 the brasses are divided into four classes: class I, so-called "High Brass" is suited especially for cold-rolling; class II, the standard common metal, can be rolled either cold or hot; class III, so-called "Low Brass," can be rolled hot only. Annealing<sup>2</sup> at  $420^{\circ}$  C. begins to cause rearrangement of distorted crystals; heating to  $600-700^{\circ}$  C. removes all internal strains; at  $800^{\circ}$  C. there is danger of burning the alloy.<sup>3</sup> Fig. 27 gives the structure of rolled common brass that worked well, Fig. 28 that of one which furnished an unsatisfactory plate; the former has a close fine grain, the latter (badly annealed) is made up of large crystals, and is weak. Other photomicrographs are given by Lewis,<sup>4</sup> Bengough-

<sup>1</sup> Gard, *Rev. Mét.*, 1909, VI, 1069 (London Congress); *Metallurgie*, 1910, VII, 651; *Proc. Inst. Assoc. Test. Mat.*, New York, 1912, II, 15.

Diegel, *Verh. Verein. Beförd. Gewerbeft.*, 1906, LXXV, 177; *Metallurgie*, 1906, III, 568.

Krom, *Met. Ind.*, 1910, VIII, 8, 111, 157, 342, 375, 459, 499; 1911, IX, 27, 123, 127; 1912, X, 20, 118, 331; 1913, XI, 18, 337.

Stilson, *Eng. Mag.*, 1913, XLV, 239.

<sup>2</sup> Moore, "Annealing Furnaces," *Met. Ind.*, 1910, VIII, 45.

<sup>3</sup> Charpy, "Contributions à l'étude des alliages," Paris, 1901, p. 1.

<sup>4</sup> *Engineering*, 1903, LXXVI, 753; *Met. Ind.*, 1903, I, 33; *J. Soc. Chem. Ind.*, 1903, XXII, 12.

TABLE 8.—INDUSTRIAL BRASSES (REGULAR)

Class	Industrial name	Cu per cent.	Zn per cent.	Color	Fracture	Malleability and ductility	U. S. Government Specifications, July 1, 1910 <sup>1</sup>
I	Red brass.....	90	10	Yellow-red.....	Vesicular.....	Malleable and ductile when cold; the prop- erties decrease with increase of zinc.	Braze metal: Cu 84-86, Zn 14-16, Fe <0.06, Pb <0.30.
	Tomback.....	85	15	Red-yellow.....	Earthy.....		
	Fine casting brass and braz- ing metal.....	80	20	Yellow.....	Earthy.....		
	Pinchbeck, Sheet brass.....	75	25	Pale yellow.....	Earthy.....		
	Fine yellow brass.....	70	30	Pale yellow.....	Earthy.....		
II	Standard yellow (common, low) brass. <sup>2</sup>	66.6	33.4	Deep yellow.....	Fibrous to coarse.....	Malleable and ductile cold or hot, usually only rolled.	Cu 64-68, Zn 32-34, Fe <2.0, Pb <3.0.
III	Common yellow brass.....	63	37	Deep yellow.....	Fibrous to coarse.....	Malleable only hot (not ductile).	Brass rods: Cu 60-63, Zn 37-40, Pb <3.
	Muntz metal <sup>3</sup> .....	60	40	Golden yellow.....	Fibrous to coarse.....	Same.....	Cast naval brass: Cu 59-63, Zn 35.5- 40.5, Sn 0.5-1.5.
	Extrusion metal <sup>4</sup> .....	55	45	Golden yellow.....	Fibrous to coarse.....	Same.....	Cu 59-62, Zn 39-41, Pb <0.6.
	White button brass.....	45	55	Pinkish gray.....	Coarsely crystalline.....	Brittle.	
IV	White brass.....	35	65	Silver gray.....	Conchoidal.....	Brittle.	
	White brass.....	10	90	Bluish white.....	Finely-granular.....	Brittle.	

<sup>1</sup> *Brass World*, 1910, VI, 397.<sup>2</sup> Bolton, "Brass Wire," *Iron Age*, 1906, LXXVIII, 1676.<sup>3</sup> Hamlet, "Decay and Corrosion of Muntz Metal," *London Min. J.*, 1907, LXXXI, 485, 523.<sup>4</sup> Johnson, "Effect of Sb, As and Bi upon Muntz Metal," *Engineering*, 1913, XCV, 2 and 3.<sup>4</sup> Sperry, "Extrusion or Squirting Process," *Brass World*, 1908, IV, 3.

Hudson,<sup>1</sup> Carpenter-Edwards<sup>2</sup>, Bengough.<sup>3</sup> Class IV, or "White Brass," includes the alloys that cannot be rolled. The so-called "Cast Brass" includes the range of composition occupied by classes II, III, and IV. It usually undergoes no mechanical treatment, hence it need not be so pure as the alloy that is to be rolled or drawn; in fact, the impurities present or purposely added make it run more smoothly, fill the mold more evenly, and permit machining more readily.

**28. Special Brass.**—The leading special brasses<sup>4</sup> are aluminum-, iron-, manganese-, tin-, and nickel-brass.

(a) **ALUMINUM BRASS (HERCULES METAL)** does not contain over 4 per cent. Al, as the presence of a larger amount renders the alloy difficult to work. The usual range of composition is Cu 67-71 per cent., Zn 31.75-25.50 per cent., Al 1.25-2.50 per cent.

Carpenter-Edwards<sup>5</sup> have investigated that part of the ternary system Cu-Zn-Al which is richest in Cu. They find that there is no ternary eutectic, that the larger part of the liquidus surface consists of two areas corresponding to  $\alpha$ - and  $\beta$ -solutions, that the  $\alpha$ -alloys undergo no transformation on cooling, but that the  $\beta$ -alloys are resolved into  $\alpha + \gamma$ , and that a thermal change takes place at 700° C. They conclude that starting from the Cu-Al-side toward the Zn-side the mechanical properties will change not suddenly, but uniformly and progressively.

Guillet,<sup>6</sup> who studied this series of alloys microscopically, concludes that 1 lb. Al can replace 3.5 lb. Zn; an alloy with 38 per cent. Zn and 2 per cent. Al, e.g., has the same structure as one with 45 per cent. Zn. The alloys are fine-grained, and give good castings which should be cooled slowly. They can be worked at lower temperatures than the corresponding Zn-Cu alloys being more malleable. The mechanical properties of a  $\frac{6}{4}\frac{0}{0}$  and a  $\frac{7}{3}\frac{0}{0}$  aluminum brass annealed are shown in Figs. 29 and 30. Their resistance to corrosion is discussed by Rowland.<sup>7</sup> The addition as a deoxidizer of 0.05 per cent. Al to ordinary brass that is to be cast in sand is helpful in obtaining clean castings; with castings to be made in metal molds the addition of Al is to be avoided.<sup>8</sup>

(b) **IRON-BRASS.**—The addition of up to 3 per cent. Fe to brass strengthens and hardens the alloy, increases the malleability when hot, and the resistance to corrosion. The constitution of these alloys has not been studied; the effect of Fe upon the structure has been investigated by Carpenter.<sup>9</sup>

<sup>1</sup> *J. Instit. Metal*, 1909, I, 89, 1910,<sup>2</sup> IV, 92; *J. Soc. Chem. Ind.*, 1908, XXVII, 1 (Muntz Metal).

<sup>2</sup> *J. Instit. Met.*, 1911, V, 127; 1912, VII, 70; 1912, VIII, 51.

<sup>3</sup> *Op. cit.*, 1912, VII, 123.

<sup>4</sup> Rosenhain, *J. Inst. Met.*, 1912, VII, 191.

<sup>5</sup> *Internat. Zt. Metallographie*, 1912, II, 209; *Rev. Mét.*, 1913, X, 429; *J. Inst. Met.*, 1912, VIII, 322; comment by Guillet, *Rev. Mét.*, 1913, X, 463.

<sup>6</sup> *Rev. Mét.*, 1905, II, 111, 1906; III, 254.

<sup>7</sup> *J. phys. chem.*, 1908, XII, 180.

<sup>8</sup> Sperry, *Met. Ind.*, 1903, I, 35.

<sup>9</sup> *J. Inst. Met.*, 1912, VIII, 66.



Sterro-, Aich and Deltametal, Tobin Bronze, and Duranametal are industrial names for this class of alloy.

*Sterrometal*<sup>1</sup> has the following range of composition: Cu 60, Zn 38-38.5, Fe 2-1.5; it represents a  $\frac{3}{4}$  brass in which part of the Zn has been replaced by Fe; it has a tensile strength of 50,000-70,000 lb. per square inch, with an elongation of from 11 to 39 per cent. in 8 in.<sup>2</sup> Sometimes a small amount of Sn is added to improve its quality; such an alloy contains Cu 55-60, Zn 34-44, Fe 2-4, Sn 1-2, and has a tensile strength ranging from 43,000 to 82,000 lb

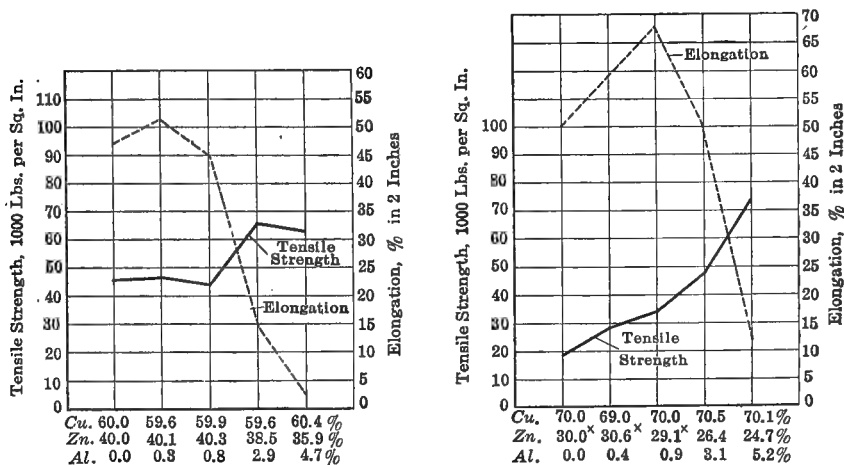


FIG. 29-30.—Mechanical properties of  $\frac{3}{4}$  and  $\frac{7}{8}$  aluminum brass.

\* These figures have been changed slightly from the originals to bring up the totals to 100 per cent.

per square inch. An alloy Cu 55.04 per cent., Zn 42.36 per cent., Fe 2.77 per cent., Sn 0.83 per cent., gave tensile strength, cast 40,320 lb., forged 76,160 lb., cold-drawn 40,320 lb.<sup>3</sup>

*Aich Metal* resembles sterrometal. Hiorns<sup>4</sup> gives Cu 58-60 per cent., Zn 36-41 per cent., Fe 0.74-1.74 per cent., Sn 0-1.02 per cent. as the range of composition.

*Delta Metal* contains usually Cu 55 per cent., Zn 41 per cent., Fe 3 per cent., Mn, etc., 1 per cent. Tetmayer's tests<sup>5</sup> gave tensile strength, cast 44,000 lb. per square inch and elongation 30-40 per cent. in  $7\frac{7}{8}$  in. These alloys are said to resist corrosion better than ordinary brass. In the manufacture, Fe is introduced by using iron-bearing Zn, rarely iron-bearing Cu.

*Tobin Bronze.*<sup>6</sup>—Two analyses gave Cu 59.00, Zn 38.40, Sn 2.16, Fe 0.11

<sup>1</sup> Guillet, *Rev. Mét.*, 1906, III, 264.

<sup>2</sup> Thurston, "A Treatise on Brasses, Bronzes, etc.," 1900, p. 415.

<sup>3</sup> *Op. cit.*, p. 368.

<sup>4</sup> "Mixed Metals," Macmillan, N. Y., 1913, p. 159.

<sup>5</sup> *Schweizerisches Gewerbeblatt*, June 8, 1889.

<sup>6</sup> Garrison, *J. Frankl. Inst.*, 1891, CXXXII, 55.

Pb 0.31 and Cu 61.20, Zn 37.14, Sn 0.90, Fe 0.18, Pb 0.35; the tensile strength showed 78,500 lb.; the elongation 15 per cent. in 2 in. and 40.5 per cent. in 8 in. The original Tobin bronze<sup>1</sup> contained Cu 58.22, Zn 39.48, Sn 2.30; it showed a tensile strength cast of 66,000 lb., rolled 79,000 lb., and cold rolled 104,000 lb. per square inch.

*Durana Metal*<sup>2</sup> contains Cu 64–78 per cent., Zn 29.50, Fe 1.51, Al 1.70, Sn and Sb 2.20. The tensile strength is 82,000 lb.; elongation 14 per cent., and elastic limit 70,000 lb.

(c) MANGANESE-BRASS.<sup>3</sup>—In the trade these alloys often go by the name of *manganese-bronze*,<sup>4</sup> a name that ought to be reserved for Cu, Sn, Mn alloys. Mn appears to harden brass, to increase the tensile strength, and to diminish the elongation; 1 lb. Mn can take the place of 0.5 lb. Cu.<sup>5</sup> However, the yellowish alloy called Parson's manganese-bronze contains only from a trace to 0.02 per cent. Mn as seen by the two following recent analyses:<sup>6</sup> cast metal, Cu 57.30, Zn 40.44, Sn 1.01, Fe 0.79, Pb none, Al 0.46, Mn trace; sheet metal, Cu 60.17, Zn 37.47, Sn 0.99, Fe 1.24, Pb trace, Al none, Mn 0.02. Its mechanical properties<sup>7</sup> cover the following range: tensile strength 81,500–90,500 lb. per square inch; elastic limit 39,300–44,750 lb.; elongation 40–26 per cent.; and reduction of area 47.5–33.0 per cent. The effects of the pouring temperature upon the size of grain and thereby upon the mechanical properties have been studied by Gillett.<sup>8</sup> The alloy is used for propeller blades, parts of guns, carriages, automobiles, valve-stems, shafting of motor-boats, etc. The specifications of the U. S. Government Bureau of Steam Engineering, of July 1, 1910,<sup>9</sup> call for Cu 57–60, Zn 37–40, Sn 0.75, Fe <1.00, Al <0.50, Mn <0.30; those of the American Society for Testing Materials:<sup>10</sup> Cu 55–60, Zn 39–45, Fe = or <2, Sn not >2, Al not >2, Mn not >2 per cent., ultimate strength not >70,000 lb. per square inch, elongation in 2 in. not <20 per cent.

(d) TIN-BRASS.—According to Johnson<sup>11</sup> Sn is only slightly soluble in  $\alpha$ -, but readily so in  $\beta$ -brass (cast); rolling and annealing help the solution in the  $\alpha$ -constituent of a  $\frac{7}{8}$  brass. Carpenter<sup>12</sup> found that 1 per cent. Sn greatly favored the formation of the  $\gamma$ -constituent. These alloys contain Cu 60–62,

<sup>1</sup> Thurston, *Tr. Am. Soc. Civ. Eng.*, 1881, XI, 1309.

<sup>2</sup> Knorre, *Zt. angew. Chem.*, 1894, 238.

<sup>3</sup> GENERAL, *Foundry*, 1905, XXVI, 116; MIXTURES, *Mel. Ind.*, 1909, VII, 173; 1910, X, 5; CASTING, *Mel. Ind.*, 1903, I, 131; 1910, VIII, 410; 1911, IX, 4, 73; *Brass World*, 1905, I, 153; 1910, VI, 79; *Foundry*, 1905, XXVI, 87; 1912, XL, 487; TESTS, *Mel. Ind.*, 1907, VII, 175; *WIRE, Brass World*, 1905, I, 255; SPECIFICATIONS, *Mel. Ind.*, 1909, VII, 1.

<sup>4</sup> Corse-Skillmann, "History" *Mel. Chem. Eng.*, 1914, XII, 113.

<sup>5</sup> Guillet, *Rev. Mét.*, 1906, III, 258.

<sup>6</sup> *Mel. Ind.*, 1909, VII, 173.

<sup>7</sup> *Op. cit.*, p. 175.

<sup>8</sup> *Tr. Am. Instit. Met.*, 1912, VI, 207.

<sup>9</sup> *Brass World*, 1910, VI, 398.

<sup>10</sup> *Year Book*, 1911, p. 135.

<sup>11</sup> *J. Inst. Met.*, 1912, VII, 201.

<sup>12</sup> *Op. cit.*, 1912, VIII, 65.

Zn 37.5-39, Sn 1-1.5 per cent. Guillet<sup>1</sup> found that 1 per cent. Sn replaced about 1.5 lb. Zn, but the amount of Sn has to be kept below 4 per cent., as otherwise the alloy becomes brittle. The main advantage of an addition of Sn is an increased resistance to corrosion. In the manufacture of the alloy the Sn is introduced into the stream of Cu-Zn as it flows from the crucible. Capp<sup>2</sup> found that the data for elastic limit obtained by the usual methods of testing are unreliable for this class of alloys, as well as for brasses and bronzes in general. The effects of Mn, Si, Cr, Wo and Va on brasses have been summarized and described by Escard,<sup>3</sup> those of Cr and Va by Carpenter.<sup>4</sup> As little as 0.04 per cent. Va<sup>5</sup> reduces the electric conductivity, but increases the elastic limit, tensile strength, and ductility from 10 to 20 per cent. According to Gin<sup>6</sup> the Ruebel alloy is prepared by melting together Cu 45-57 parts, Zn 40, and (Va, Cu, Al, Fe) 3-15. The commercial Cu-Va alloy contains 3 per cent. Va, but is difficult to obtain free from Fe and Al.

(e) NICKEL-BRASS.—The mechanical properties of brass are improved by an addition of Ni;<sup>7</sup> it can replace 1.2 parts of Zn.

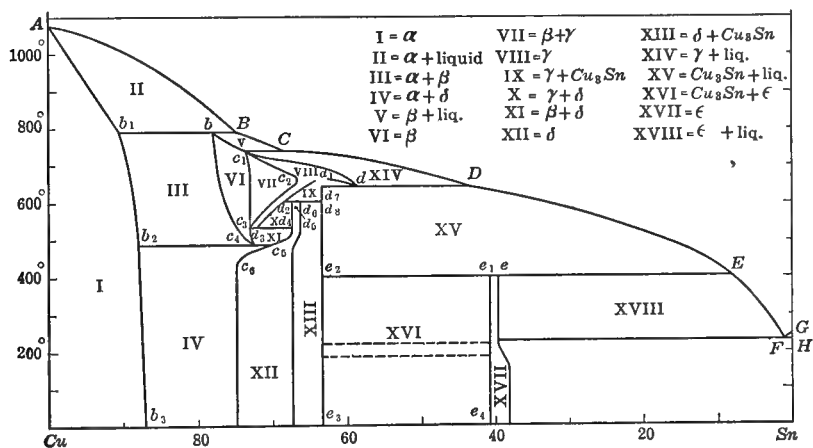


FIG. 31.—Alloy-series Cu-Sn, bronze.

Guillet,<sup>8</sup> who has studied the effects of Ni upon brass, finds that small additions of Ni make brass easier to work cold, and that additions up to 10 per cent. improve the mechanical properties.

**29. Bronze<sup>9</sup> (Cu and Sn).** In General.—The complicated constitution of

<sup>1</sup> *Rev. Mét.*, 1906, III, 264.

<sup>2</sup> *J. Am. Soc. Mech. Eng.*, 1910, XXXII, 373; *Iron Age*, 1910, LXXXVI, 628; *J. Inst. Met.*, 1910, IV, 310.

<sup>3</sup> *Génie Civil*, 1909, LV, 74, 85; *Oest. Zt. Berg. Hüttenw.*, 1910, LVIII, 201, 215.

<sup>4</sup> *J. Inst. Met.*, 1912, VIII, 165.

<sup>5</sup> Norris, *J. Frankl. Inst.*, 1911, CLXXI, 580.

<sup>6</sup> *Metall-Erz.*, 1913, X, 502.

<sup>7</sup> Guillet, *Compt. rend.*, 1912, CLV, 1512; *J. Inst. Met.*, 1913, IX, 213.

<sup>8</sup> *Rev. Mét.*, 1913, X, 1130.

<sup>9</sup> Thurston, *op. cit.*

bronzes has been studied by Stansfield,<sup>1</sup> Heycock and Neville,<sup>2</sup> Roberts-Austen,<sup>3</sup> Sheperd and Blough,<sup>4</sup> Giolitti and Tovante.<sup>5</sup> Following the freezing-point curve of Sheperd and Blough, shown in Fig. 31, bronzes may contain five solid solutions,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ , and the chemical compound  $\text{Cu}_3\text{Sn}$ ; the compositions and colors are given in Table 9.

TABLE 9.—CONSTITUENTS OF BRONZE

Constituent	Nature and Composition	Color
$\alpha$	Solid solution of Cu and Sn with from 0 to 13 per cent. Sn	Reddish-yellow to yellow.
$\beta$	Solid solution of Cu and Sn with from 22 to 27 per cent. Sn	Yellow.
$\gamma$	Solid solution of Cu and Sn with from 27 to 57 per cent. Sn	White.
$\delta$	Solid solution of Cu and Sn with from 24 to 33 per cent. Sn	White.
$\epsilon$	Solid solution of Cu and Sn with from 33 to 59 per cent. Sn	White.
$\text{Cu}_3\text{Sn}$	Chemical compound, 61.5 per cent. Cu, 37.5 per cent. Sn	White.

The liquidus is shown in *A, B, C, D, E, F, G*, the solidus in *A, b<sub>1</sub>, b, c<sub>1</sub>, d, d<sub>1</sub>, e<sub>2</sub>, e<sub>1</sub>, e, F, H*. The six components and their combinations give bronzes characteristic structures, represented by fields I–XVIII. Field I is the region of pure  $\alpha$ -crystals; in field II,  $\alpha$ -crystals are stable in contact with the mother-metal; in III crystals

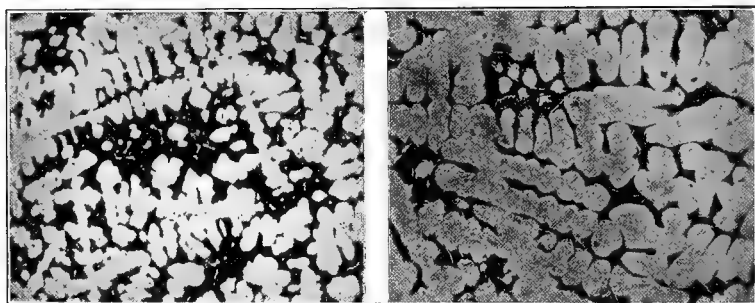


Fig. 32.—Alloy chilled at 777° C.

Fig. 33.—Alloy cooled slowly to 546° C. and then chilled.

FIGS. 32–33.—Cast bronze with 15.6 per cent. Sn;  $\alpha$ -crystals light,  $\beta$ -crystals dark.

$\alpha$  and  $\beta$  form a conglomerate; at 486° C.  $\beta$ -crystals break down into  $\alpha$  and  $\delta$ , and furnish the stable forms  $\alpha$  and  $\delta$  for field IV; in field V,  $\beta$ -crystals are stable in contact with mother-metal; field VI is the region for pure  $\beta$ -crystals, as is VII for a conglomerate of  $\beta + \gamma$ , and VIII the region for pure  $\gamma$ ; the solid solution  $\delta$  in field XII (once considered to be  $\text{Cu}_4\text{Sn}$ ), formed by a transformation in the solid of  $\gamma + \text{Cu}_3\text{Sn}$  in field IX, is stable below 600° C. and so on. The meaning of the two horizontal lines at 218 and 182° C. in field XVI has not yet been interpreted.

<sup>1</sup> *Third Rep. Alloys Research Comm.*, 1895, 269.

<sup>2</sup> *Phil. Trans. A.*, 1897, CLXXXIX, 42.

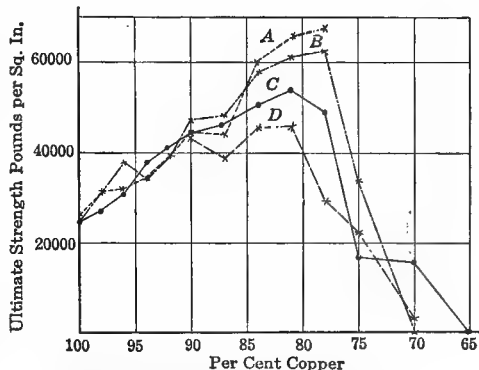
<sup>3</sup> *Fourth Rep. Alloys Research Comm.*, 1897, 67; Suppl. by Campbell *Fifth Rep.*, 1901, 1211.

<sup>4</sup> *J. phys. chem.*, 1906, X, 630.

<sup>5</sup> *Gazz. chim. ital.*, 1908, XXXVIII, 2, 209; *Rev. Mét.*, 1909, VI, 476.

Two photomicrographs of Heycock and Neville, Figs. 32-33, show light  $\alpha$ - and dark  $\beta$ -crystals in an alloy with 15.6 per cent. Sn. The alloy represented by Fig. 32, was chilled at 777° C.; that by Fig. 33 slowly cooled to 546° C. and then chilled.

The range of composition of the bronzes that are of importance in engineering is much smaller than that of brasses; 80 per cent. represents the lowest figure for Cu, or 70 per cent. if bell metal be included. The transformations that are possible in the region 100 to 70 per cent. Cu show that the physical properties of these alloys must be considerably affected by heat treatment. The ultimate strength and elongation<sup>1</sup> of bronzes, both cast and annealed, are shown in Figs. 34 and 35. In Fig. 34 the tensile strength is seen to increase with an addition of Sn until the maximum is reached with about 80 per cent. Cu; the strength of an alloy with 70 per cent. Cu is very small, falling to about 16,000 lb. per square inch. Heat treatment<sup>2</sup> does not affect alloys with from 100 to 86 per cent. Cu, as these are homogeneous, consisting exclusively of  $\alpha$ -crystals. With alloys containing from 86 to 76 per cent. Cu the case is different. Annealed at 400° C. (curve D) they consist of  $\alpha$ - +  $\delta$ -crystals (Fig. 31); while holding at 540° C. and then chilling in water (curve B) has changed  $\alpha$  +  $\delta$  into  $\alpha$  +  $\beta$ . The  $\frac{78}{22}$  alloy with  $\alpha$  +  $\delta$  structure shows a tensile strength of 45,000 lb. per square inch; the same with  $\alpha$  +  $\beta$  structure, one of 67,000 lb. The curve C for cast bronze with from 86 to 76 per cent. Cu lies between curves B and D, as the



- A. Heated to low red, water-quenched.  
B. Held one week at 540° C, water-quenched.  
C. Tested as cast.  
D. Held one week at 400° C, furnace-cooled.

FIG. 34.—Tensile strength of cast bronze.

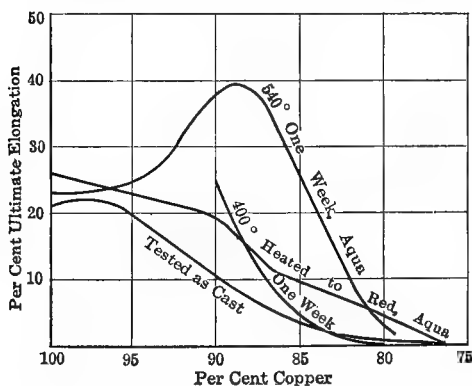


FIG. 35.—Ductility of cast bronze. Aqua = water-quenched.

cooling was so quick as to allow only part of  $\alpha$  +  $\delta$  to change into  $\alpha$  +  $\beta$ , hence such a cast bronze can contain all three constituents  $\alpha$ ,  $\beta$ , and  $\delta$ . An alloy with 70 per cent. Cu may contain  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  crystals, depending upon the

<sup>1</sup> Sheperd-Upton, *J. phys. chem.*, 1905, IX, 441; *Metallurgie*, 1906, III, 29; *Rev. Mét.*, 1906, III, 8.

<sup>2</sup> Grenet, *Rev. Mét.*, 1911, VIII, 108; *Metallurgie*, 1911, VIII, 543.

rate of cooling. The constituent  $\delta$  makes the alloy brittle; whenever it forms more than 70 per cent. of the alloy the strength decreases rapidly.

In Fig. 35 the differences in ductility between cast and annealed bronzes are clearly shown. In cast bronzes with from 100 to 80 per cent. Cu the ductility, excepting a slight rise, decreases with an increase of Sn; heating such

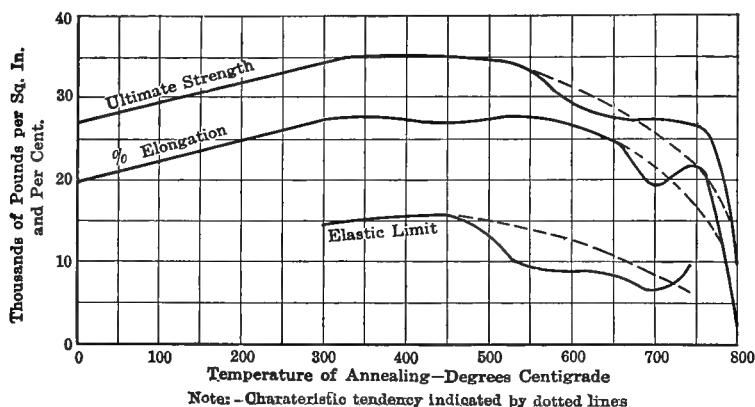


FIG. 36.—Mechanical changes of  $\frac{95}{5}$  bronze at varying temperatures.

bronzes to 540° C. and then quenching in water increases the ductility by 5 per cent. The greatest ductility is reached with a bronze of 90 to 88 per cent. Cu, a composition which lies very close to the maximum of Sn in  $\alpha$ -crystals.

The changes in the leading mechanical properties of cast bronzes, of the compositions  $\frac{95}{5}$ ,  $\frac{91}{9}$  and  $\frac{87}{13}$ , when tested between zero and 800° C. are shown

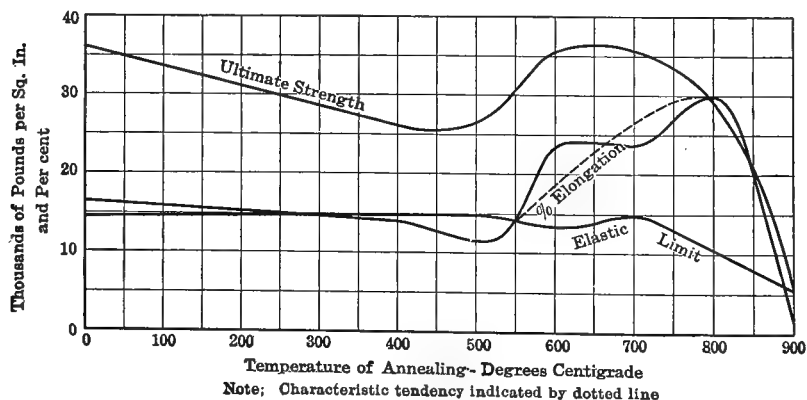


FIG. 37.—Mechanical changes of  $\frac{91}{9}$  bronze at varying temperatures.

in Figs. 36, 37 and 38.<sup>1</sup> The alloys  $\frac{95}{5}$  and  $\frac{91}{9}$  have  $\alpha$  as sole constituent, but show a difference in behavior when pulled in the testing machine. In the  $\frac{87}{13}$  alloy, consisting when annealed of  $\alpha + \delta$ , the change into  $\alpha + \beta$  near 500° C. is

<sup>1</sup> Guillet, L., "Trempe, Recuit, Revenu," Dunod, Paris, 1909, p. 572.

clearly marked by the mechanical tests.<sup>1</sup> The relation between mechanical properties and heat treatment of drawn bronzes has been studied by Goerens-Dumont,<sup>2</sup> and Guillet,<sup>3</sup> some physical properties by Wyss,<sup>4</sup> the specific heats by Chappell.<sup>5</sup> Bronzes occlude little gas;<sup>6</sup> they resist corrosion, less when rich in Cu than when rich in Sn.<sup>7</sup> Giolliti and Ceccareli,<sup>8</sup> studying bronzes with up to 10 per cent. Sn, found that heat treatment affected the corrosion of the  $\alpha$ -solution, that the  $\alpha+\beta$  alloy was more quickly attacked than the  $\alpha$

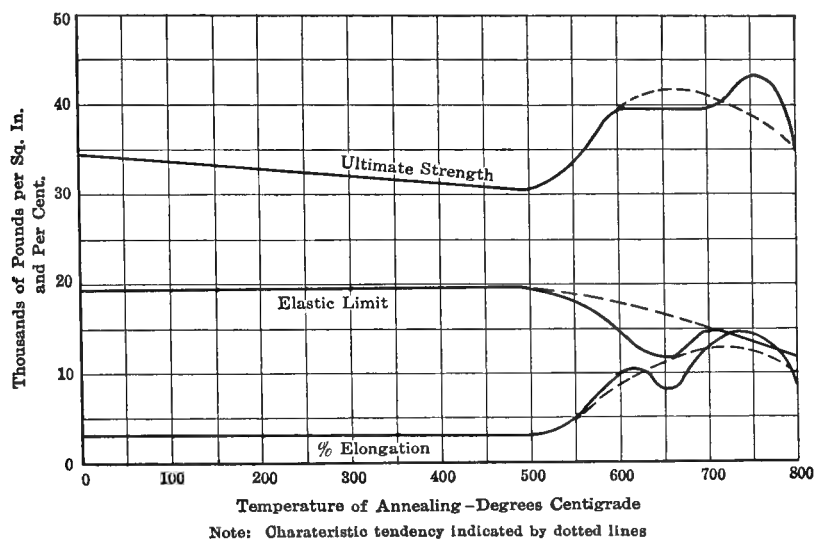


FIG. 38.—Mechanical changes of 88 bronze at varying temperatures.

alone, and that the greater the difference in composition between center and edge of a crystal the more rapid the attack. Impurities greatly affect the properties.<sup>9</sup> Shrinkage<sup>10</sup> is lessened by Zn,<sup>11</sup> increased by Co, Al, Si, Fe, and Ni.<sup>12</sup> Tensile strength is considerably lowered by Sb or much Zn;<sup>13</sup> it is raised by Co, Ni, Mn, and Fe; it is lowered by a rise in temperature.<sup>14</sup> Machining is made

<sup>1</sup> Portevin, *Rev. Mét.*, 1903, X, 677.

Robin, *op. cit.*, 1913, X, 764.

<sup>2</sup> *Ferrum*, 1912-13, X, 21.

<sup>3</sup> *Rev. Mét.*, 1913, X, 769.

<sup>4</sup> *Ferrum*, 1912-13, X, 167.

<sup>5</sup> *Op. cit.*, 1913, X, 271.

<sup>6</sup> Guillemain-Delachanal, *Rev. Mét.*, 1911, VIII, 1.

<sup>7</sup> Carpenter-Edwards, *Met. Chem. Eng.*, 1911, IX, 63.

<sup>8</sup> *Gazzetta chim. Ital.*, XXXIX, 557; *J. Inst. Met.*, 1911, VI, 333.

<sup>9</sup> Miller, *Metallurgie*, 1912, IX, 63.

<sup>10</sup> Turner-Haughton, *J. Inst. Met.*, 1911, VI, 192.

<sup>11</sup> Wüst, *Metallurgie*, 1909, VI, 769; *Iron Age*, 1910, LXXXV, 790.

<sup>12</sup> Chamberlain, *J. Inst. Met.*, 1913, X, 193.

<sup>13</sup> Guillet-Revillon, *Rev. Mét.*, 1910, VII, 429; *Metallurgie*, 1911, VIII, 582.

<sup>14</sup> Johnson, *Met. Chem. Eng.*, 1911, IX, 399.

easier by Sb and Pb and more difficult by Mn and Ni; Pb in excess of 0.15 per cent. affects the strength; and leady bronzes<sup>1</sup> are readily attacked by boiling water and steam. Patina formation is lessened by Zn and Al, intensified by Co, Ni, Sb, Fe, Si, and P. Fe gives the alloy a lighter color. Hardening is discussed by Grenet,<sup>2</sup> the wearing qualities by Portevin-Nussbaum.<sup>3</sup>

In the manufacture, oxidation has to be avoided. Heyn and Bauer<sup>4</sup> found that  $\text{Cu}_2\text{O}$  was readily reduced,  $2\text{Cu}_2\text{O} + \text{Sn} = 4\text{Cu} + \text{SnO}_2$ , the  $\text{SnO}_2$  separating in large crystals which, insoluble in the alloy, rendered it less fluid. Jolibois-Thomas<sup>5</sup> made similar observations. Large charges are melted in reverberatory furnaces, small ones in crucibles;<sup>6</sup> in either case oxidation has to be avoided. Even a crucible and a charcoal cover do not absolutely prevent oxidation, as some  $\text{Cu}_2\text{O}$  is formed. This is most pronounced with alloys containing over 84 per cent. Cu.

A powerful reducing agent, such as P or preferably P-Sn, is sometimes used to counteract the oxidation. This alloy,<sup>7</sup> containing about 5 per cent. P, is prepared by charging a graphite crucible with stick P, covering with 1 in. of charcoal, filling with granulated (flake) tin (1 P: 10 Sn), giving a charcoal cover, putting on a cover and luting it, and bringing gently to a low-red in a pot-furnace. The P being volatilized is taken up by the Sn. When the flame of burning P disappears, the charge is finished, the alloy stirred, skimmed, and poured into small ingot molds set in water. Portevin<sup>8</sup> found that in making some castings in a strongly reducing atmosphere, the ingots became porous, and required the addition of an oxidizing agent.

TABLE 10.—REGULAR AND SPECIAL BRONZES

Class	Name	Composition, per cent.					Color	Fracture	Malleability and ductility.
		Cu	Sn	P	Si	Mn			
Regular	Malleable bronze...	98-94	2-6	.....	.....	.....	Red to reddish yellow.	Vesicular.	Rolled and hammered.
	Gun metal.....	92-88	8-12	.....	.....	.....	Reddish yellow to dirty yellow.	Crystalline to fine-grained.	Difficult to roll, hard.
	Bell metal.....	80-75	20-25	.....	.....	.....	Yellowish gray to gray.	Fine-grained.	Cannot be rolled, hard.
	Speculum metal....	70-65	30-35	.....	.....	.....	Ash-gray to white.	Conchoidal.	Brittle, steely, susceptible of perfect polish.
Special	Phosphor bronze...	90-91	9-8	< 1	.....	.....	Reddish yellow.		
	Silicon bronze.....	88	10	.....	.....	■	White.		
	Manganese bronze..	.....	.....	.....	.....	0-tr	.....		

<sup>1</sup> Bailey, *J. Soc. Chem. Ind.*, 1905, XLV, 52.

<sup>2</sup> *Compt. rend., Soc. Ind. Min.*, 1911, XIV, 138; *J. Inst. Met.*, 1911, VI, 334.

<sup>3</sup> *Sixth Internat. Congr. Testing Mat.*, 1912; *Ferrum*, 1913, X, 379.

<sup>4</sup> *Zt. anorg. Chem.*, 1905, XLV, 520; *Metallurgie*, 1905, II, 190, 201.

<sup>5</sup> *Rev. Mét.*, 1913, X, 1264.

<sup>6</sup> Sperry, "Casting Brass for Rolling," *Brass World*, 1911, VII, 3.

<sup>7</sup> *Met. Ind.*, 1903, I, 36; 1909, VIII, 3.

<sup>8</sup> *Rev. Mét.*, 1913, X, 944.



In a fusion for bronze, the Cu is charged, covered with charcoal, and melted; then melted bronze-scrap is added, and lastly the necessary Sn warmed to near its melting-point. Alloys with from 4 to 6 per cent. Sn are cast in metal, those richer in Sn in sand molds. A crucible will stand from 25 to 30 charges. Table 10 gives the compositions of some regular and special bronzes.

**30. Regular Bronze.**—The four general alloys under regular bronzes include many commercial varieties which contain other constituents beside Cu and Sn.<sup>1</sup>

**1. MACHINERY BRONZES.**—These alloys (Thurston's Kalchoids<sup>2</sup>) used as bearings contain from 2 to 8 per cent. Zn, the Sn being added after the brass has been prepared. Ordinary bearing metal consists of Cu 81–87 per cent., Sn 19–13 per cent.; the addition of Zn makes the alloy cast better and resist corrosion more effectively, but it increases the hardness, and with this the rate of wear. Nevertheless it is much used. Thus Cu 81, Sn 17, Zn 2; Cu 84, Sn 12, Zn 4; Cu 82, Sn 10, Zn 8 are not uncommon mixtures. In general, a good bearing metal<sup>3</sup> must have at least two constituents, a hard one to support the load, and a soft one to act as a plastic support for the hard grains. Bearing metals are of two kinds, *White* or *Antifriction Metals*<sup>4</sup> in which Pb, Sb, and Sn(Cu), and *Bearing Bronzes*<sup>5</sup> in which Cu and Sn(Zn. and Pb) are the leading metals. As the rate of wear in a bronze bearing diminishes with the decrease of Sn and the increase of Pb, the latter has replaced a considerable portion of the former; thus the Pennsylvania Railroad's plastic bronze (Ajax plastic metal) consists<sup>6</sup> of Cu 64, Sn 5, Pb 30, Ni 1, the Ni being necessary to cause rapid setting and thus to counteract liquation.<sup>7</sup> Thurston<sup>8</sup> considers the strongest ternary bronzes to have the composition Cu 58–54, Sn 1.5–2.5, Zn 44–40.

**2. GUN METAL**<sup>9</sup> has lost its former importance; the Uchatius gun contains Cu 92, Sn 8. Modern gun metal contains some Zn, *e.g.*, Cu 88, Sn 10, Zn 2; Cu 86, Sn 10, Zn 4; Cu 87, Sn 8, Zn 5.<sup>10</sup> Specifications of the Bureau of Steam

<sup>1</sup> Guillet-Revillon, *Rev. Mét.*, 1909, VI, 1251 (report to Copenhagen Internat. Congr. Testing Mat.).

<sup>2</sup> Structural Study by Hoyt, *J. Inst. Met.*, 1913, X, 235.

<sup>3</sup> Clamer, *J. Frankl. Inst.*, 1903, CLVI, 49; *Proc. Am. Soc. Test. Mat.*, 1907, VII, 302; *Met. Ind.*, 1909, VII, 407; 1910, VIII, 209.

Job, *J. Frankl. Inst.*, 1900, CXLIX, 439; *Iron Age*, May 31, 1900, p. 6.

Price, *Proc. A. I. Mech. E.*, 1904–05, XXVI, 669; *Iron Trade Rev.*, Aug. 3, 1905, p. 32.

Allan, *Met. Ind.*, 1910, VIII, 67.

<sup>4</sup> Charpy, "Contributions à l'étude des alliages," p. 201; *Metallographist*, 1899, II, 9.

Behrens-Baucke, *op. cit.*, 1900, III, 4.

<sup>5</sup> Allan, *Met. Ind.*, 1909, VII, 243, 321; 1910, VIII, 67, 289; 1911, IX, 155, 295, 476.

Clamer, *op. cit.*, 1909, VII, 407; 1910, VIII, 208; 1911, IX, 418.

Heyn-Bauer, *Stahl u. Eisen*, 1911, XXXI, 1416.

<sup>6</sup> Clamer, *loc. cit.*; *Met. Ind.*, 1911, IX, 114.

<sup>7</sup> Jones, High-lead bronzes, *Met. Ind.*, 1906, IV, 81.

<sup>8</sup> *Op. cit.*, p. 446.

<sup>9</sup> Primrose, *J. Inst. Met.*, 1910, IV, 248; 1913, IX, 158; "Mechanical Properties," *Brass World*, 1913, IX, 176.

<sup>10</sup> McWilliam, A. and Longmuir, P., "General Foundry Practice," Lippincott, Philadelphia, 1912, p. 321; *J. I. and St. I.*, 1903, I, 462.

Engineering U. S. Government, July 1, 1910, call for Cu 87-89, Sn 9-11, Zn 1-3, Fe < 0.06, Pb < 0.20.

3. BELL METAL, as the name indicates, is very resonant; large bells contain 25 per cent. Sn, small ones 15 per cent. Beside the main constituents bell metal sometimes contains small amounts of Zn and Ag. The tone of a bell depends more upon its shape than its composition.

4. STATUARY BRONZE contains Cu 90-78, Sn 2-4, Zn 10-18 per cent., sometimes small amounts (1-4 per cent.) of Pb. Variations in composition are governed by the color (oranges to yellows) desired for the casts; the amount of Sn is kept low to avoid brittleness, that of Zn within given limits, as its whitening power is great.

5. COIN OR MEDAL BRONZE contains Cu 90-96, Sn 10-4 per cent., sometimes 1 per cent. Zn.

6. SPECULUM (MIRROR) METAL, once used for the manufacture of reflectors for telescopes, has been replaced by silvered glass. The constituents  $\delta$  and  $\text{Cu}_3\text{Sn}$  are the cause of its susceptibility of a fine polish.

**31. Special Bronze.** (1) PHOSPHOR BRONZE.—The addition of 1 per cent. P to bronze increases greatly the strength and decreases the elongation. However, comparatively little metal going by the name of phosphor bronze contains more than a trace of P, the alloys P-Sn or P-Cu having been used in the manufacture to prevent or correct oxidation and thus to increase the good mechanical properties.

The form in which P is present in real phosphor bronze has not been definitely settled. Guillet<sup>1</sup> believes that P enters the  $\alpha$ -constituent with alloys containing < 9 per cent. Sn; Law<sup>2</sup> states that alloys with > 9 per cent. Sn show the  $\delta$ -constituent and the compound  $\text{Cu}_3\text{P}$  which may form a eutectic mixture; Hudson-Law<sup>3</sup> believe they have found a ternary eutectic. According to the chemical and mechanical investigations of Philip,<sup>4</sup> phosphor bronzes may be grouped according to their uses in three classes: *Heavy castings*: Cu 90-92, Sn 7.4-9.7, P 0.3-0.6, tensile strength > 34,000 lb., elongation 20 per cent. in 2 in.; *Rod, Sheet, Wire*: Cu 91.5-97.5, Sn 8.4-2.25, P 0.1-0.25, when unannealed tensile strength 60,000 lb., elongation 10 per cent. in 2 in., when annealed 40,000 lb. and 40 per cent. in 2 in.; *Bearings*: Cu 84.5-89.1, Sn 14.5-10.1, P 0.8-1.0 and possibly higher. The specifications of the U. S. Bureau of Steam Engineering of July 1, 1910, call for Cu 80-90, Sn 6-8, Zn 2-14, P 0.30, Fe < 0.06, Pb < 0.20.

The main advantages of phosphor bronze are its strength, its resistance to corrosion,<sup>5</sup> and, if high enough in P, its hardness to resist abrasion combined with a low friction-coefficient, both of which make it suited for bearings. The method of manufacture<sup>6</sup> differs little from that of other alloys.

<sup>1</sup> "Les Alliages Métalliques," Dunod, Paris, 1906, p. 556.

<sup>2</sup> Law, E. F., "Alloys," Lippincott, Philadelphia, 1909, p. 155.

<sup>3</sup> *J. Inst. Met.*, 1910, III, 161.

<sup>4</sup> *J. Inst. Met.*, 1909, I, 164; *Foundry*, 1908-09, XXXIII, 231.

<sup>5</sup> *Brass World*, 1910, VI, 398; Curry, "Electrolytic Corrosion," *Electrochem. Met. Ind.*, 1906, IV, 223.

<sup>6</sup> Sperry, *Brass World*, 1907, III, 399.

2. **SILICON BRONZE.**<sup>1</sup>—This is a bronze to which has been added during the melt about 10 per cent. silicon-copper as a deoxidizing agent in order to reduce any  $\text{SnO}_2$  that has been formed. No Si or only 0.05 per cent. remains in the alloy. The greater electric conductivity makes silicon bronze preferable to phosphor-bronze for telephone wires. The electric conductivity curves of bronze of Ledoux<sup>2</sup> show two sharp cusps at  $\text{Cu}_4\text{Sn}$  and  $\text{Cu}_3\text{Sn}$ .

3. **MANGANESE BRONZE.**—Manganese plays a double rôle; it acts as a deoxidizer; and gives the Cu-Sn alloy special mechanical properties. Guillet<sup>3</sup> prepared the alloys given in Table II and subjected them to mechanical tests.

TABLE II.—MANGANESE BRONZES

Composition, per cent.			Tensile strength, lb. per sq. in.	Elastic limit, lb. per sq. in.	Elongation in 4 in., per cent.
Cu	Sn	Mn			
90.93	8.82	none	31,200	11,800	23
90.12	9.20	trace	34,200	11,400	28
87.64	10.41	1.67	27,200	12,800	20
89.38	8.61	0.69	20,800	12,400	7.5
85.87	8.76	3.10	1,500	15,000	.....

Tough, malleable manganese bronze consists of Cu 75–76, Mn 16–17, Sn 5–6 per cent.; it is brass-yellow. An addition of less than 5 per cent. Al increases the strength and elastic limit, and gives it a whitish color. Sometimes Zn in amounts less than 5 per cent. is added to the alloy. A common composition is Cu 88, Sn 10, Mn 2. This alloy is ductile, hard, tough, and reddish white.

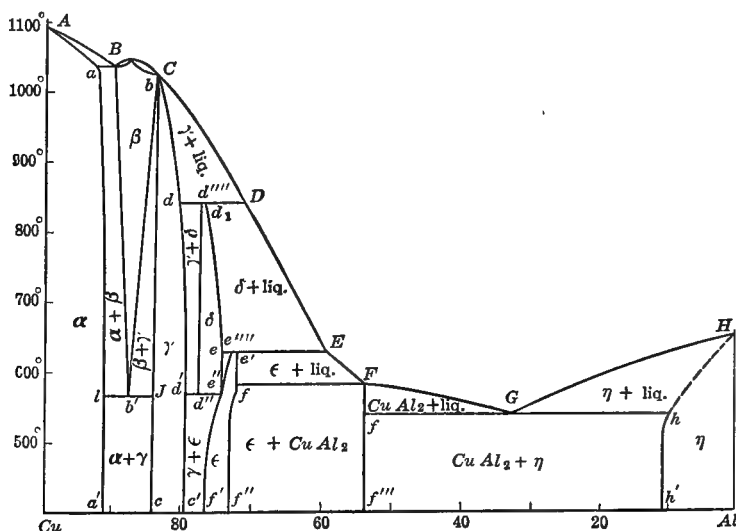


FIG. 39.—Alloy-series Cu-Al, aluminum bronze.

<sup>1</sup> Sperry, *op. cit.*, 1905, I, 75.<sup>2</sup> *Compt. Rend.*, 1912, CLV, 35; *J. Inst. Met.*, 1912, VIII, 335.<sup>3</sup> *Génie Civil*, 1905, XLVII, 147.

**32. Aluminium Bronze (Cu-Al).**—The older investigations into the constitution by Le Chatelier,<sup>1</sup> Campbell-Mathews,<sup>2</sup> Guillet,<sup>3</sup> Dejean<sup>4</sup> have been supplemented by the more recent work of Carpenter-Edward,<sup>5</sup> Curry<sup>6</sup> and Gwyer.<sup>7</sup> According to the curve of Curry, Fig. 39, who obtained his data from heating instead of cooling-curves and thus avoided all under-cooling, there exist six solid solutions  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ ,  $\eta$ , the chemical compound,  $\text{CuAl}_2$ , an eutectic mixture,  $\text{CuAl}_2 + \eta$ , and two transformation-temperatures below which  $\beta$  and  $\delta$  are unstable.<sup>8</sup> The nature, limits of composition, and color of crystals are given in Table 12.

TABLE 12.—COMPONENTS OF ALUMINUM BRONZE

Component	Nature	Per cent. copper at deg. C.			Color
		1000°	700°	500°	
$\alpha$	Solid solution of Cu and Al	100-92	100-91	100-91	Copper-red to golden yellow
$\beta$	Solid solution of Cu and Al	90-85	88.5-87	Unstable	Yellow.
$\gamma$	Solid solution of Cu and Al	84-83	84-80	84-79	White.
$\delta$	Solid solution of Cu and Al	Liquid	87-85	Unstable	White.
$\epsilon$	Solid solution of Cu and Al	Liquid	Liquid	73.5-76.0	White
$\eta$	Solid solution of Cu and Al	Liquid	Liquid	0-11	White.
$\text{Cu Al}_2$	Chemical compound.....	Liquid	Liquid	53.7 <sup>a</sup>	White.
Eutectic	$\text{Cu Al}_2 + \eta$ .....	Liquid	Liquid	32 <sup>b</sup>	White.

<sup>a</sup>Freezes at 585° C.

<sup>b</sup>Freezes at 543° C.

The tensile strength and ductility of alloys with from 100 to 85 per cent. Cu and from 0 to 25 per cent. Cu, as determined by Curry and Woods<sup>9</sup> are given in Figs. 40-41, in which curve *A* represents the chill-cast alloy, *B* the alloy annealed below 565° C., and *C* the alloy annealed and quenched above 565° C.<sup>10</sup> The alloys containing from 25 to 85 per cent. Cu are too brittle to be of any technical value. The tensile strength of Cu is gradually increased by the presence of Al until the Cu content has fallen to 92 per cent., when the curve rises rapidly to a maximum with 90 per cent. Cu and then falls. The alloy is made up largely of  $\alpha$ -crystals, up to 91 per cent. Cu, when  $\beta$ -crystals begin to appear. Cast and annealed alloys with up to 92 per cent. Cu show

<sup>1</sup> *Bull. Soc. d'Enc.*, 1895, x, 573.

<sup>2</sup> *J. Am. Chem. Soc.*, 1902, XXIV, 253.

<sup>3</sup> *Rev. Mét.*, 1905, II, 568; Summary, *op. cit.*, 1908, v, 413.

<sup>4</sup> *Op. cit.*, 1906, III, 240.

<sup>5</sup> *Eighth Rep. Alloys Research Comm.*, 1907, 57; *Rev. Mét.*, 1908, v, 425; *Metallurgie*, 1907, IV, 253.

<sup>6</sup> *J. phys. chem.*, 1907, XI, 425; *Metallurgie*, 1908, v, 540.

<sup>7</sup> *Zt. anorg. Chem.*, 1908, LVII, 113.

<sup>8</sup> Structure of  $\alpha + \gamma$  in alloys with Cu 84-90 percent.: Hanemann-Merica, *Internat. Zt. Metallographie*, 1913, IV, 209; Structure of  $\beta$ : Portevin, *op. cit.*, 1913, IV, 257.

<sup>9</sup> *J. phys. chem.*, 1907, XI, 462.

<sup>10</sup> Edwards *Internat. Zt. Metallographie*, 1912, III, 179.

Portevin-Arnon, *Compt. rend.*, 1912, CLIV, 511.

little difference in tensile strength when the curves *A*, *B*, and *C* begin to separate, the 90-per cent. alloy chilled showing 100,000 lb. tensile strength.

Ductility shows a greater variation than does tensile strength. With the addition of Al to Cu, ductility rises at first quickly, then more slowly until

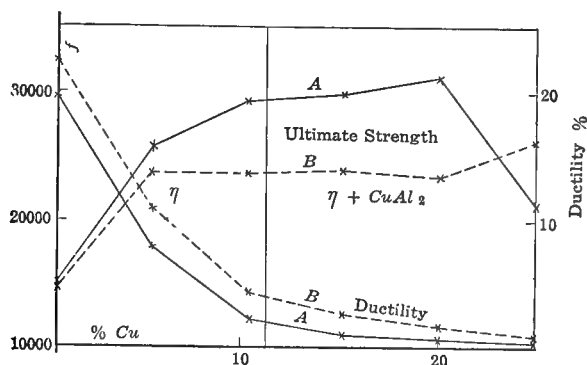
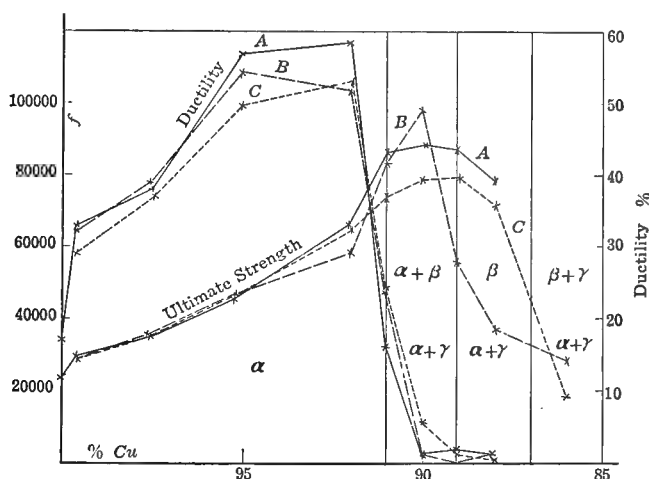


FIG. 40-41.—Tensile strength and ductility of copper-aluminum alloys.

the alloy with 95 per cent. Cu has been reached, when the approximate parallelism of the three curves ceases. Alloys with from 92 to 95 per cent. Cu have ductilities of from 50 to 60 per cent. In alloys with from 92 to 91 per cent. Cu, ductility drops from 57.5 to 16 per cent., and a further 1.2 per cent. with the 90-per cent. alloy, showing the stiffening effect of  $\beta$ -crystals. The



FIGS. 40-41.—Tensile strength and ductility of copper-aluminum alloys.

strongest alloy contains 90 per cent. Cu., the most ductile 92-95 per cent. Cu when chilled above  $566^{\circ}\text{C}$ .<sup>1</sup>

Fig. 41 shows the effects of additions of Cu to Al; the tensile strength is at first rapidly increased until the Al has taken up 5 per cent. Cu, then more

<sup>1</sup> Carpenter-Edwards, "Resistance to internal pressure," *Met. and Chem. Eng.*, 1911, IX, 63.

gradually until a maximum is reached with 20 per cent. Cu. The ductility-curve shows a steady decrease with additions of Cu, more rapid at first than later on. The most dependable alloy is the one with 10 per cent. Cu, which lies on the edge of the  $\eta$ -field.

Electric conductivity is treated by Wilson<sup>1</sup> and Broniewski.<sup>2</sup>

Formerly Cu-Al alloys were prepared by the Cowles electrothermic process; this gave way to the melting together of the two component metals. The greatest difficulty met with in the manufacture<sup>3</sup> is oxidation of the surface, causing dirty castings; the only remedy known is to stir as little as possible. Upon adding Al to melted Cu there is a rise in temperature of from 150 to 250° C. due to the heat of solution.<sup>4</sup>

Cu with from 3 to 5 per cent. Al loses its reddish color. The  $\frac{9}{10}$  alloy is yellow with a greenish tinge, is malleable cold, but much more when hot; does not change its color when exposed to moist air, but tarnishes when heated; is not attacked by salt water,  $\text{NH}_3$ ; nor  $\text{H}_2\text{S}$ ; is slowly attacked by dilute  $\text{H}_2\text{SO}_4$ ;  $\text{HCl}$  dissolves the Al.

The  $\frac{9}{10}$  alloy containing 1-2 per cent. Si is stronger and much less ductile than the normal alloy; a small amount of iron greatly increases the strength.

Cu-Al-Mn alloys have been investigated by Rosenhain and Lantsberry.<sup>5</sup> They find that the effect of Mn upon Cu is similar to that of Al.

The effects of additions of small amounts of P upon the mechanical properties of the  $\frac{9}{10}$  and  $\frac{9}{10}$  alloys have been studied by Read.<sup>6</sup>

**33. Minor Alloys.**—Cu and Ti are treated by Rossi,<sup>7</sup> Guillet,<sup>8</sup> and Bensell;<sup>9</sup> the effects of Cr, W, and Va are reviewed by Escard;<sup>10</sup> of Hg by Guntz-de Greift.<sup>11</sup>

<sup>1</sup> *Engineering*, 1904, LXXVIII, 33.

<sup>2</sup> *Proc. Internat. Assoc. Test. Mat.*, June, 1912.

<sup>3</sup> Sperry, *Met. Ind.*, 1904, II, 3.

<sup>4</sup> Richards, *Electrochem. Ind.*, 1903, I, 575.

<sup>5</sup> *Ninth Report Alloys Research Comm.*, 1910, pp. 119-339.

<sup>6</sup> *J. Inst. Met.*, 1913, X, 344.

<sup>7</sup> *Electrochem. Met. Ind.*, 1908, VI, 257; 1909, VII, 88.

<sup>8</sup> "Étude industrielle des alliages métalliques," Dunod-Pirat, Paris, 1906, pp. 774 *et seq.*

<sup>9</sup> *Metall-Erz*, 1914, XI, 10, 46.

<sup>10</sup> *Génie Civil*, 1909, LV, 74, 85; *Oest Zt. Berg. Hüttenw.*, 1910, LVIII, 201, 215.

<sup>11</sup> *Compt. rend.*, 1912, CLIV, 213, 357.

## CHAPTER V

### COPPER COMPOUNDS

**34. Cuprous Oxide,  $\text{Cu}_2\text{O}$**  (88.81 per cent. Cu;  $127.2 \text{ Cu}_2 + 16 \text{ O} = 143.2 \text{ Cu}_2\text{O} + 43,800 \text{ cal.}$ ).—It occurs as cuprite; is formed by heating solid copper in air above  $1060^\circ \text{ C.}$ , at which temperature the  $\text{CuO}$  formed is decomposed;<sup>1</sup> or by keeping melted copper above  $1200^\circ$  in air when it becomes covered with fused  $\text{Cu}_2\text{O}$ ; or by roasting copper sulphide. The color of  $\text{Cu}_2\text{O}$  is cherry-red when compact and the luster metallic; it often forms isometric crystals; the powder is carmine-red; the melting-point is given as  $1166^\circ \text{ C.}$ <sup>2</sup> and as  $1200^\circ$ ;<sup>3</sup> it is somewhat soluble in melted Cu., §8.

Prolonged heating between  $500$  and  $1000^\circ \text{ C.}$  changes  $\text{Cu}_2\text{O}$  into  $\text{CuO}$ ; heating to  $1952^\circ \text{ C.}$  splits this into  $\text{Cu}_2\text{O} + \text{O}$ ; the reaction  $2\text{Cu}_2\text{O} = 2\text{Cu}_2 + \text{O}$  occurs at  $2208^\circ$ .<sup>4</sup>  $\text{Cu}_2\text{O}$  is readily reduced to metal by  $\text{H}$   $147^\circ \text{ C.}$ ,<sup>5</sup>  $\text{C}$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_2$ ; the reduction by  $\text{C}$  begins at about  $500^\circ \text{ C.}$ <sup>6</sup> Heating with  $\text{Cu}_2\text{S}$  gives  $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightleftharpoons 6\text{Cu} + \text{SO}_2$ ; this reaction begins<sup>7</sup> at about  $450^\circ \text{ C.}$ , and is finished<sup>8</sup> at about  $1100^\circ$ . Schenck-Hempelmann<sup>9</sup> have shown by experiments in an evacuated tube that the reactions  $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightleftharpoons 6\text{Cu} + \text{SO}_2$  and  $2\text{CuSO}_4 + \text{Cu}_2\text{S} \rightleftharpoons 2\text{Cu}_2\text{O} + 3\text{SO}_2$  are reversible, the second taking place at a lower temperature than the first. In furnace-work in which there is practically no partial pressure of  $\text{SO}_2$ , both reactions can proceed only from left to right; and the second will be of minor importance, as  $\text{CuSO}_4$  begins to give off  $\text{SO}_3$  at  $670^\circ \text{ C.}$  and is completely decomposed at  $736^\circ \text{ C.}$ <sup>10</sup> Heating with 1.5 parts by weight of  $\text{PbO}$  forms a readily fusible mixture; heating with  $\text{FeS}$  gives  $2\text{Cu}_2\text{O} + 3\text{FeS} = (\text{Cu}_2\text{S})_2 \cdot \text{FeS} + 2\text{FeO}$ ; the reaction begins at  $270$ – $280^\circ \text{ C.}$  and the speed increases with the temperature.<sup>11</sup>  $\text{Cu}_2\text{O}$  is insoluble in  $\text{H}_2\text{O}$ ; solubilities and reactions in wet processes are expressed by  $\text{Cu}_2\text{O} + \text{NH}_3 + \text{O} = x\text{CuO} \cdot \text{NH}_3$ ;  $\text{Cu}_2\text{O} + 2\text{HCl} = \text{Cu}_2\text{Cl}_2 + \text{H}_2\text{O}$  (addition of  $\text{H}_2\text{O}$  precipitates  $\text{Cu}_2\text{Cl}_2$ );  $\text{Cu}_2\text{O} + \text{H}_2\text{SO}_4 = \text{Cu} + \text{CuSO}_4 + \text{H}_2\text{O}$ ;  $\text{Cu}_2\text{O} + \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} = 2\text{CuSO}_4 + \text{Fe}_2\text{SO}_6 + \text{H}_2$ ;  $\text{Cu}_2\text{O} + \text{Fe}_2$ .

<sup>1</sup> Wöhler, *Zt. Electrochem.*, 1906, XII, 784.

<sup>2</sup> Heyn, *Mitth. Kgl. Versuchsanst.*, 1900, XVIII, 320.

<sup>3</sup> Slade-Farrow, *Proc. Roy. Soc. A.*, 1912, LXXXVII, 524.

<sup>4</sup> Stahl, *Metallurgie*, 1907, IV, 690.

<sup>5</sup> Otin, *Metallurgie*, 1912, IX, 98.

<sup>6</sup> Doeltz-Graumann, *op. cit.*, 1907, IV, 421.

<sup>7</sup> Doeltz-Graumann, *loc. cit.*

<sup>8</sup> Heyn-Bauer, *Metallurgie*, 1906, III, 83.

<sup>9</sup> *Metall-Erz*, 1913, X, 283.

See also Stubbs, *J. Soc. Chem. Ind.*, 1913, XXXII, 31.

<sup>10</sup> See Kernel-roasting, § 54.

<sup>11</sup> Juschewitsch-Schilowski, *Metallurgie*, 1912, IX, 543.

$(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 = 2\text{CuSO}_4 + 2\text{FeSO}_4 + \text{H}_2\text{O}$ ; <sup>1</sup>  $3\text{Cu}_2\text{O} + 2\text{FeCl}_2 = \text{Cu}_2 + 2\text{Cu}_2\text{Cl}_2 + \text{Fe}_2\text{O}_3$ .

**35. Cupric Oxide** ( $\text{CuO}$ : 79.8 per cent. Cu;  $63.6\text{Cu} + 16\text{O} = 79.6\text{CuO} + 37,700\text{ cal.}$ ) occurs as tenorite (melanconite); is formed by heating in air  $\text{Cu}_2\text{O}$  below  $1000^\circ\text{C.}$ ; by dead-roasting copper sulphide; by heating  $\text{CuCO}_3$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{CuSO}_4$ , precipitated  $\text{Cu}(\text{OH})_2$ . It is brownish-black to black; has no luster; may form isometric crystals; is decomposed into  $\text{Cu}_2\text{O} + \text{O}$  by heating above  $1069^\circ$ ,<sup>2</sup> into  $\text{Cu} + \text{O}$  at  $2208^\circ$ ;<sup>3</sup> is decomposed by Fe at about  $740^\circ\text{C.}$ ;<sup>4</sup> is readily reduced to metal by H, C, CO,  $\text{C}_x\text{H}_y$ , as is  $\text{Cu}_2\text{O}$ , the reduction by H begins at  $250^\circ\text{C.}$ , by CO at about  $160^\circ$  and is 97 per cent. at  $325^\circ$ ,<sup>5</sup> by  $\text{CH}_4$  at a red heat.<sup>6</sup> Heating with  $\text{Cu}_2\text{S}$  gives  $\text{Cu}_2\text{S} + 2\text{CuO} = 4\text{Cu} + \text{SO}_2$ ; the temperature limits are similar to those of  $\text{Cu}_2\text{O}$ ; heating with 1.8 parts by weight of PbO gives a readily fusible mixture; heating with FeS gives  $6\text{CuO} + 4\text{FeS} = 3\text{Cu}_2\text{S} + 4\text{FeO} + \text{SO}_2$ . It is insoluble in  $\text{H}_2\text{O}$ ; soluble in  $\text{NH}_3$ ,  $(\text{NH}_4)_2\text{CO}_3$ , partly soluble in hot  $\text{NH}_4\text{Cl}$ ; readily soluble in dilute acids. In wet processes the following reactions are recognized:  $3\text{CuO} + 2\text{FeCl}_2 = \text{Cu}_2\text{Cl}_2 + \text{CuCl}_2 + \text{Fe}_2\text{O}_3$ ;  $6\text{CuO} + 4\text{FeCl}_3 = 6\text{CuCl}_2 + 2\text{Fe}_2\text{O}_3$ ;  $3\text{CuO} + 6\text{FeSO}_4 + 3\text{H}_2\text{O} = 3\text{CuSO}_4 + 2\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2(\text{SO}_4)_3 + 6\text{H}$ ;  $3\text{CuO} + \text{Fe}_2(\text{SO}_4)_3 = 3\text{CuSO}_4 + \text{Fe}_2\text{O}_3$ ;  $3\text{CuO} + 3\text{Fe}_2(\text{SO}_4)_3 = 3\text{CuSO}_4 + \text{Fe}_2\text{O}_3 \cdot 2\text{Fe}_2(\text{SO}_4)_3$ . Cupric hydroxides are formed by precipitation from dilute solutions of  $\text{CuO}$ -salts.

**36. Cupric Carbonate** ( $\text{CuCO}_3$ : 51.45 per cent. Cu;  $63.6\text{Cu} + 12\text{C} + 48\text{O} = 123.6\text{CuCO}_3 + 146,100\text{ cal.}$ ).—The neutral salt is not known. Basic salts occur as malachite and azurite; they are formed by precipitation of  $\text{CuO}$ -solutions with alkali carbonates, and are readily decomposed, by heating, into  $\text{CuO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

**37. Copper Silicates.**—These occur only as cupric hydrous silicates, diopside, and chrysocolla.

**CUPROUS SILICATES.**—Otin<sup>7</sup> has shown that by heating  $\text{Cu}_2\text{O}$  and  $\text{SiO}_2$  in varying proportions, there are formed four silicates,  $5\text{Cu}_2\text{O} \cdot \text{SiO}_2$ ,  $3\text{Cu}_2\text{O} \cdot \text{SiO}_2$ ,  $2\text{Cu}_2\text{O} \cdot \text{SiO}_2$ , and  $1\text{Cu}_2\text{O} \cdot \text{SiO}_2$ . They begin to form at  $600^\circ\text{C.}$  and sinter at  $900^\circ$ ; this is especially noticeable with  $2\text{Cu}_2\text{O} \cdot \text{SiO}_2$  and  $1\text{Cu}_2\text{O} \cdot \text{SiO}_2$ . Single pieces have a bluish-black color and show crystallinity; the powder is brownish-red to light brown. The silicates are brittle, the hardness decreasing as the copper-content increases. With the specific gravity of  $\text{Cu}_2\text{O}$  as 5.744, this figure falls with increase of  $\text{SiO}_2$  and reaches 4.995 with  $\text{Cu}_2\text{O} \cdot 70.36 + \text{SiO}_2 \cdot 29.63$ . Tests with  $2\text{Cu}_2\text{O} \cdot \text{SiO}_2$  and  $1\text{Cu}_2\text{O} \cdot \text{SiO}_2$  as to the chemical behavior showed that these compounds are soluble in concentrated  $\text{HNO}_3$  and dilute  $\text{CH}_3\text{CO}_2\text{H}$ ; readily so in  $\text{HCl}$ ; slowly in  $\text{H}_2\text{SO}_4$ ; and that they are attacked by  $\text{NH}_3$ . The reduction

<sup>1</sup> Thompson, *Electrochem. Ind.*, 1904, II, 227.

<sup>2</sup> Slade-Farrow, *Proc. Roy. Soc. A.*, 1912, LXXXVII, 524; *J. Inst. Met.*, 1913, IX, 207; *Met. Chem. Eng.*, 1913, XI, 105; *Zt. Electrochem.*, 1912, XVIII, 817.

<sup>3</sup> Stahl, *Metallurgie*, 1907, IV, 690.

<sup>4</sup> Friedrich, *Stahl u. Eisen*, 1911, XXXI, 2040.

<sup>5</sup> Howe, *Tr. A. I. M. E.*, 1878-79, VII, 444.

<sup>6</sup> Other data: Fay-Secker-Lane-Ferguson, *Min. Ind.*, 1911, XX, 472.

<sup>7</sup> *Metallurgie*, 1912, IX, 92.



in a current of H begins a little above  $147^{\circ}$  C.; in a current of CO it begins at  $180^{\circ}$ . The speed of reaction increases rapidly with rise of temperature; at  $220$ – $245^{\circ}$  all the  $\text{Cu}_2\text{O}$  is reduced to Cu.

Cuprous silicates are readily decomposed by FeO, CaO, *e.g.*,  $\text{Cu}_4\text{SiO}_4 + 2\text{FeO} = 2\text{Cu}_2\text{O} + \text{Fe}_2\text{SiO}_4$ ; by Fe, FeS,  $\text{Cu}_2\text{S}$  as indicated by  $\text{Cu}_4\text{SiO}_4 + 2\text{Fe} = 4\text{Cu} + \text{Fe}_2\text{SiO}_4$ , by  $\text{Cu}_4\text{SiO}_4 + 2\text{FeS} = 2\text{Cu}_2\text{S} + \text{Fe}_2\text{SiO}_4$ , by  $\text{Cu}_4\text{SiO}_4 + \text{Cu}_2\text{S} = 6\text{Cu} + \text{SiO}_2 + \text{SO}_2$ .

CUPRIC SILICATES.—These are formed by heating in air CuO and  $\text{SiO}_2$ ; they form a brownish-black pasty mass; in the presence of a reducing agent some CuO will be reduced to  $\text{Cu}_2\text{O}$  and cause the formation of a blood-red slag.

**38. Copper Sulphides.**—1. CUPROUS SULPHIDE ( $\text{Cu}_2\text{S}$ : 79.87 per cent. Cu;  $127.2 \text{ Cu}_2 + 32 \text{ S} = 159.2 \text{ Cu}_2\text{S} + 20,300 \text{ cal.}$ ) occurs as chalcocite; is readily formed by repeated heating of Cu filings and S; by immersing Cu in a bath of boiling S and heating the product with exclusion of air; and by allowing S-vapor to act upon red-hot Cu. It is bluish-black, amorphous or crystalline according to the mode of preparation, melts at  $1121^{\circ}$  C.;<sup>1</sup> an excess of S over the theoretical lowers the melting point.<sup>2</sup> Other melting points given are  $1085$ ,<sup>3</sup>  $1091$ ,<sup>4</sup>  $1105$ ,<sup>5</sup>  $1123$ ,<sup>6</sup>  $1127$ ,<sup>7</sup>  $1155$ ,<sup>8</sup>  $1130$ ,<sup>9</sup>  $1127$  and  $1130$  are the best figures. It forms an eutectic with Cu (§17); its intermetallic compounds are discussed under matte (§119). Next to Mn it has a stronger affinity for S than has any other metal.<sup>10</sup> It is stable at elevated temperature in a neutral atmosphere, and is not oxidized by air at ordinary temperature. When heated with access of air,<sup>11</sup>  $\text{SO}_2$  is given off at temperatures ranging from  $430$  to  $680^{\circ}$  C. depending upon the size of grain. The sample glows at the same time and is converted slowly at a gradually increasing temperature into CuO; during the roast it passes through the stages of  $\text{Cu}_2\text{O}$  and  $\text{CuSO}_4$ . Its tendency to sinter while roasting must be attributed to some compound of  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{O}$ . Laboratory experiments by Warlimont<sup>12</sup> showed that in 4 hr. 42 per cent. of the Cu was converted into  $\text{CuSO}_4$ . The presence of FeS greatly increases sulphatization (§214). Air forced through fused  $\text{Cu}_2\text{S}$  at a temperature of about  $1150^{\circ}$  C. decomposes it into Cu and  $\text{SO}_2$  (converter process, §157);  $\text{CO}_2$  oxidizes it slowly at a red heat (Hampe). CO has no effect. At a red heat H decomposes it slowly but completely;<sup>13</sup> water-vapor

<sup>1</sup> Friedrich, *Metallurgie*, 1904, IV, 672.

<sup>2</sup> Friedrich, *op. cit.*, 1905, V, 52.

<sup>3</sup> Röntgen, *op. cit.*, 1906, III, 479.

<sup>4</sup> Bodländer-Idaszewski, *Zt. Electrochem.*, 1905, XI, 161; *Eng. Min. J.*, 1905, LXXIX, 827.

<sup>5</sup> Bornemann, *Metallurgie*, 1909, VI, 623.

<sup>6</sup> Baykoff-Troutneff, *Rev. Mét.*, 1909, VI, 519.

<sup>7</sup> Heyn-Bauer, *Metallurgie*, 1903, III, 73.

<sup>8</sup> Hofman-Caypless-Harrington, *Tr. A. I. M. E.*, 1907, XXXVIII, 142.

<sup>9</sup> Hayward, *Bull. A. I. M. E.*, January, 1914, p. 45.

<sup>10</sup> Stütz, *Metallurgie*, 1907, IV, 697.

<sup>11</sup> Friedrich, *Metallurgie*, 1909, VI, 169.

<sup>12</sup> *Metallurgie*, 1909, VI, 132.

<sup>13</sup> Hampe, *Chem. Z.*, 1885, IX, 1442.

Haupt, *Eng. Min. J.*, 1904, LVIII, 511.

Heyn-Bauer, *Metallurgie*, 1906, III, 85.

does the same at a white heat.<sup>1</sup> Fusing with Fe may decompose  $\text{Cu}_2\text{S}$  or not, as the reaction  $\text{Cu}_2\text{S} + \text{Fe} \rightleftharpoons \text{Cu}_2 + \text{FeS}$  is reversible and incomplete in either case.<sup>2</sup> The experiments of Gibb-Philp<sup>3</sup> and Baykoff-Troutneff<sup>4</sup> show that the direction of the reaction depends upon the relative amounts of reagents used. Gibb-Philp decomposed  $\text{Cu}_2\text{S}$ , fused in a crucible, with an iron rod, *i.e.*, a large excess of iron, and obtained a copper bottom (not analyzed) and a matte with Cu 60.6, Fe 17.8, S 21.7 per cent.; while Baikoff-Troutneff, using a mixture of 90 per cent. Cu and 10 per cent. FeS, obtained a button with Cu 94.49 per cent., Fe 5.32 per cent., S not determined, and a matte with Cu 60.7, Fe 17.6, S 21.7 per cent., *i.e.*, one of the same composition as Gibb-Philp. Juschkevitch<sup>5</sup> goes one step further. He found that upon heating  $\text{Cu}_2\text{S}$  and FeS there was formed already at 200° C. the compound  $(\text{Cu}_2\text{S})_2 \cdot \text{FeS}$ , the speed of the reaction increasing with the temperature. Heating  $\text{Cu}_2\text{S}$  with Fe gave at 400° C. the same compound,  $3\text{Cu}_2\text{S} + \text{Fe} = (\text{Cu}_2\text{S})_2 \cdot \text{FeS} + \text{Cu}$ . Reversing conditions, the reaction  $4\text{Cu} + 3\text{FeS} = (\text{Cu}_2\text{S})_2 \cdot \text{FeS} + \text{Fe}$  took place again at 400° C. In both cases the speed of the reaction increased with the temperature. He proved the existence of  $(\text{Cu}_2\text{S})_2 \cdot \text{FeS}$  in copper matte; this is substantiated by the freezing-point curve of Bornemann-Schreyer<sup>6</sup> discussed in §119. Juschkevitch thus is in agreement with his predecessors as regards reversibility of the reaction, but gives a different form to the equation. The system  $\text{Cu}_2\text{S}-\text{Cu}_2\text{Cl}_2$  has been studied by Truthe<sup>7</sup> who found that an eutectic with 16 per cent.  $\text{Cu}_2\text{S}$  was formed, which solidified at 392° C. Heating  $\text{Cu}_2\text{S}$  with 20 times its weight of PbO causes all the S to be oxidized.<sup>8</sup>

$\text{Cu}_2\text{S}$  is practically insoluble in  $\text{H}_2\text{O}$ , slowly soluble in  $\text{NH}_3$ . Cold  $\text{HNO}_3$  splits it into CuS and Cu, hot  $\text{HNO}_3$  dissolves it with separation of S, hot concentrated HCl dissolves it slowly with evolution of  $\text{H}_2\text{S}$ . Concentrated  $\text{H}_2\text{SO}_4$  forms CuS,  $\text{CuSO}_4$  and  $\text{SO}_2$ ; dilute  $\text{HSO}_4$  in the presence of air acts very slowly.

In wet processes the following reactions are common:  $\text{Cu}_2\text{S} + 2\text{Fe}_2(\text{SO}_4)_3 = 2\text{CuSO}_4 + 4\text{FeSO}_4 + \text{S}$ ;<sup>9</sup>  $\text{Cu}_2\text{S} + 2\text{FeCl}_3 = \text{Cu}_2\text{Cl}_2 + 2\text{FeCl}_2 + \text{S}$ ;  $\text{Cu}_2\text{S} + 2\text{CuCl}_2 = 2\text{Cu}_2\text{Cl}_2 + \text{S}$ .  $\text{Cu}_2\text{S}$  is a good electric conductor; it is not completely decomposed by pyro-electrolysis<sup>10</sup> being split into non-conducting CuS and S; suspended in an acid electrolyte of  $\text{CuSO}_4$ , it is decomposed into Cu<sub>2</sub> and S (Borchers-Franke-Günther process, § 247).

2. CUPRIC SULPHIDE (CuS: Cu 66.4, S 33.6 per cent.; 63.6 Cu + 32 S =

<sup>1</sup> Gautier, *Compt. rend.*, 1906, CXLII, 1465.

<sup>2</sup> Röntgen, *Metallurgie*, 1906, III, 479.

Schütz, *op. cit.*, 1907, IV, 663.

<sup>3</sup> *Tr. A. I. M. E.*, 1906, XXXVI, 665.

<sup>4</sup> *Rev. Mét.*, 1909, VI, 535.

<sup>5</sup> *Metallurgie*, 1912, IX, 543.

<sup>6</sup> *Metallurgie*, 1909, VI, 619.

<sup>7</sup> *Zt. anorg. Chem.*, 1912, LXXVI, 161; *Rev. Mét. Extr.*, 1913, X, 378.

<sup>8</sup> Percy, "Metallurgy," 1861, p. 262.

<sup>9</sup> Thompson, *Electrochem. Ind.*, 1904, II, 27.

<sup>10</sup> Bodländer-Idaszewski, *Zt. Electrochem.*, 1905, XI, 163; *Eng. Min. J.*, 1905, LXXIX, 827.

95.6 CuS + 10,100 cal.) occurs as covellite; is formed in the dry way by heating Cu in boiling S; in the wet way by precipitation from cupric solutions with  $\text{H}_2\text{S}$  as a brownish-black precipitate which sulphatizes readily on exposure to air. It is soluble in  $\text{HNO}_3$  and  $\text{HCl}$ ; insoluble in dilute  $\text{H}_2\text{SO}_4$ , caustic alkali, and fixed-alkali sulphide; slightly soluble in  $\text{NH}_4\text{S}$ ; it decomposes silver salts  $\text{Ag}_2\text{SO}_4 + \text{CuS} = \text{Ag}_2\text{S} + \text{CuSO}_4$ .

**39. Cupric Sulphate (Blue Vitriol)** ( $\text{CuSO}_4 + 5 \text{ aq.}$ : Cu 31.8,  $\text{SO}_3$  32.1,  $\text{H}_2\text{O}$  36.1 per cent.; Cu 25.40 per cent.;  $63.6 \text{ Cu} + 32\text{S} + 64\text{O} = 159.6 \text{ CuSO}_4 + 181,700 \text{ cal.}$ , in dilute solution 197,200 cal.) occurs as chalcantite; is formed by a sulphatizing roast of  $\text{Cu}_2\text{S}$  or  $\text{CuSi}$  by dissolving Cu in hot dilute  $\text{H}_2\text{SO}_4$  in the presence of air; by the combined action of  $\text{SO}_2$ , air, and steam upon finely-divided Cu (Rössler process<sup>1</sup>); by electrolytic solution of anode copper with dilute  $\text{H}_2\text{SO}_4$  as electrolyte; by solution of CuO in hot dilute  $\text{H}_2\text{SO}_4$ ; and by the action of  $\text{Fe}_2(\text{SO}_4)_3$  upon  $\text{Cu}_2\text{S}$ ,  $\text{Cu}_2\text{O}$ , CuO.

It forms sky-blue triclinic crystals, and mixed crystals with the isomorphous  $\text{FeSO}_4 + 7 \text{ aq.}$ ; it slowly weathers and disintegrates by prolonged exposure to atmosphere through a partial loss of  $\text{H}_2\text{O}$ , and becomes whitish.

Heating  $\text{CuSO}_4 + 5 \text{ aq.}$  in a current of dry air<sup>2</sup> converts it between 27 and 30° C. into sky-blue  $\text{CuSO}_4 + 3 \text{ aq.}$ , which is changed between 93 and 99° into pale-blue  $\text{CuSO}_4 + 1\text{H}_2\text{O}$ , and this gives up its molecule of  $\text{H}_2\text{O}$  at 150° with the formation of white  $\text{CuSO}_4$ . The anhydrous salt is converted at 341° into  $8\text{CuO} \cdot 3\text{SO}_3$  to the limit of 5.87 per cent.; at 653° orange-colored  $2\text{CuO} \cdot \text{SO}_3$  begins to be formed, the dissociation becoming energetic at 670°; the final decomposition into black CuO and  $\text{SO}_3$  begins at 704° and becomes pronounced at 736° C.

In a reducing roast with charcoal<sup>3</sup> the reaction  $2\text{CuSO}_4 + 2\text{C} = \text{Cu}_2\text{O} + 2\text{SO}_2 + \text{CO}_2 + \text{CO}$  takes place below 650° C. The reactions  $\text{CuSO}_4 + \text{Cu}_2\text{S} = \text{Cu}_3 + 2\text{SO}_2$ ;<sup>4</sup>  $2\text{CuSO}_4 + \text{Cu}_2\text{S} = 2\text{Cu}_2\text{O} + 3\text{SO}_2$ ;<sup>4</sup> and  $4\text{CuSO}_4 + \text{Cu}_2\text{S} = 6\text{CuO} + 5\text{SO}_2$  said to take place at elevated temperatures are problematical in metallurgical furnaces owing to the dissociation of  $\text{CuSO}_4$ . The salt  $\text{CuSO}_4 + 5 \text{ aq.}$  is soluble in  $\text{H}_2\text{O}$ . Its solubility at different temperatures is shown in Table 13.

Table 14 shows the specific gravities<sup>5</sup> and concentrations of blue vitriol solutions at 18° C.

The electric conductivity of mixtures of blue vitriol and sulphuric acid solutions<sup>6</sup> is given in Tables 15 and 16.

In practical work most strengths of solutions are given in terms of per centages. To convert the values in Table 15 into these units Table 16 may be used.

<sup>1</sup> Hofman, "General Metallurgy," 1913, p. 882.

<sup>2</sup> Hofman-Wanjukow, *Tr. A. I. M. E.*, 1912, XLIII, 523; complete reference to earlier work is given.

<sup>3</sup> Scherr, *School Mines Quart.*, 1899-1900, XXI, 66.

Howe, *op. cit.*, 1900-01, XXII, 381.

<sup>4</sup> See §§ 54, 127.

<sup>5</sup> Relations of specific gravity and degrees Beaumé scale, see Hofman, "General Metallurgy," 1913, p. 505.

<sup>6</sup> Richardson-Taylor, *Met. Chem. Eng.*, 1911, IX, 536.

TABLE 13.—SOLUBILITY OF BLUE VITRIOL IN WATER

At 100 gm. H <sub>2</sub> O° C. dissolve	0°	15°	25°	30°	40°	50°	60°	70°	80°	90°	100°
Gm. CuSO <sub>4</sub> . . . . .	14.9	19.3	22.3	25.5	29.5	33.6	39.0	45.7	53.5	62.7	73.5
Gm. CuSO <sub>4</sub> +5 aq. . . . .	23.3	30.2	34.9	39.9	46.2	52.6	61.1	71.6	83.8	98.2	115.0

TABLE 14.—SPECIFIC GRAVITIES AND CONCENTRATIONS OF BLUE-VITRIOL SOLUTIONS AT 18° C

Specific gravity	Per cent. of CuSO <sub>4</sub> +5 aq.	Per cent. of CuSO <sub>4</sub>	Specific gravity	Per cent. of CuSO <sub>4</sub> +5 aq.	Per cent. of CuSO <sub>4</sub>
1.0063	1	.637	1.1063	16	10.200
1.0126	2	1.275	1.1135	17	10.837
1.0190	3	1.912	1.1208	18	11.474
1.0254	4	2.550	1.1281	19	12.111
1.0319	5	3.187	1.1354	20	12.750
1.0384	6	3.825	1.1427	21	13.387
1.0450	7	4.462	1.1501	22	14.025
1.0516	8	5.100	1.1585	23	14.662
1.0582	9	5.737	1.1659	24	15.300
1.0649	10	6.375	1.1738	25	15.938
1.0716	11	7.012	1.1817	26	16.574
1.0785	12	7.650	1.1898	27	17.211
1.0854	13	8.287	1.1980	28	17.848
1.0923	14	8.925	1.2063	29	18.486
1.0993	15	9.562	1.2146	30	19.125

TABLE 15.—ELECTRIC CONDUCTIVITY OF CuSO<sub>4</sub>+5AQ AND H<sub>2</sub>O IN RECIPR. OHMS PER C.M.

Gr. H <sub>2</sub> SO <sub>4</sub> per 100 c.c.		At 25° C.					At 45° C.					
			0	5	10	15	20	0	5	10	15	20
CuSO <sub>4</sub> +5aq grams per 100 c.c.	{	gms.										
		0	.....	0.208	0.410	0.565	0.683	.....	0.246	0.492	0.683	0.839
		5	0.053	0.204	0.388	0.531	0.646	0.0205	0.242	0.461	0.643	0.791
		10	0.0221	0.195	0.350	0.500	0.600	0.0294	0.222	0.422	0.606	0.738
		15	0.0343	0.189	0.338	0.458	0.558	0.0468	0.217	0.381	0.545	0.690
		20	0.0423	0.182	0.319	0.433	.....	0.0574	0.212	0.378	0.521	0.643

TABLE 16.—CONVERSION TABLE

Percentage			Grams per 100 c.c.			Gram-equi- valent per 1000 c.c.
Cu	CuSO <sub>4</sub>	CuSO <sub>4</sub> +5aq	Cu	CuSO <sub>4</sub>	CuSO <sub>4</sub> +5aq	
1.00	2.5	3.91	1.04	2.56	4.0	0.321
2.00	5.0	7.82	2.09	5.25	8.2	0.658
3.99	10.0	15.64	4.41	11.05	17.4	1.387
5.99	15.0	23.46	6.97	17.50	27.4	2.194
6.98	17.5	27.37	8.37	22.00	32.9	2.631
H <sub>2</sub> SO <sub>4</sub>			H <sub>2</sub> SO <sub>4</sub>			H <sub>2</sub> SO <sub>4</sub>
5			5.15			1.05
10			10.7			2.18
15			16.5			3.38
20			22.8			4.66

Addition of  $\text{CuSO}_4$  to  $\text{H}_2\text{SO}_4$  increases the conductivity of the mixture if the  $\text{H}_2\text{SO}_4$  is less than 3 g. per 100 c.c.; it decreases if the  $\text{H}_2\text{SO}_4$  exceeds this amount. If the  $\text{H}_2\text{SO}_4$  is just 3 gm. per 100 c.c., the addition of a little  $\text{CuSO}_4$  to the solution of  $\text{H}_2\text{SO}_4$  has no effect upon the conductivity of the mixture.

Metallic Cu is precipitated from  $\text{CuSO}_4$  solutions by Fe and other electro-positive metals;  $\text{Cu}(\text{OH})_2$  by alkali and alkali earths;  $\text{Cu}_2\text{S}$  by  $\text{H}_2\text{S}$ , alkali and alkali earth sulphides. Electrolytically  $\text{CuSO}_4$  is split into  $\text{Cu}^{++}$  and  $\text{SO}_4^{--}$ ; the e.m.f. required with an insoluble anode is 1.48 volts.

**40. Cuprous Chloride** ( $\text{Cu}_2\text{Cl}_2$ : Cu 64.16 per cent.; 63.5 Cu+35.5 Cl=99  $\text{CuCl}+35,400$  cal.), occurs as nantokite. It is formed with some  $\text{CuCl}_2$  by the action of Cl upon Cu at ordinary temperature; of HCl gas upon Cu at a dark-red; of Cl upon Cu at a low temperature, and by heating  $\text{CuCl}_2$  ( $\text{Cl}+\text{CuCl}_2\rightleftharpoons\text{CuCl}_2$ ); by boiling Cu in an acid solution of  $\text{CuCl}_2$ ; by the reaction  $3\text{CuO}+2\text{FeCl}_2=\text{CuCl}_2+\text{Cu}_2\text{Cl}_2+\text{Fe}_2\text{O}_3$ . It is a white powder which is quickly darkened by the action of day light, when moist, with the formation of  $\text{Cu}_2\text{O}\cdot\text{CuCl}$ . It melts at  $434^\circ\text{C}$ .; is volatile at  $340^\circ\text{C}$ .;<sup>1</sup> forms with  $\text{Cu}_2\text{O}$  an eutectic mixture;<sup>2</sup> heated with  $\text{Ca}(\text{OH})_2$  and C to the melting-point of  $\text{CaCl}_2+\text{aq}$ , it gives<sup>3</sup>  $\text{Cu}_2+\text{CaCl}_2+\text{H}_2\text{O}+\text{CO}$ .

The fused salt is a good conductor of electricity, its conductivity at  $140^\circ\text{C}$ . per c.c. in recipr. ohms is at  $440^\circ-0.2084$ , at  $490^\circ-0.3960$ . It is insoluble in  $\text{H}_2\text{O}$ , soluble in HCl and metallic chloride solutions. The solubility in brine<sup>4</sup> is given in Table 17.

TABLE 17.—SOLUBILITY OF  $\text{Cu}_2\text{Cl}_2$  IN BRINE

Solution of NaCl	$\text{Cu}_2\text{Cl}_2$ dissolved, per cent.		
	At $90^\circ\text{C}$ .	At $40^\circ\text{C}$ .	
Saturated.....	16.9	11.9	8.9 per cent. at $11^\circ\text{C}$ .
15 per cent.....	10.3	6.0	3.6 per cent. at $14^\circ\text{C}$ .
5 per cent.....	2.6	1.1	.....

The electric conductivity of saturated solutions of  $\text{Cu}_2\text{Cl}_2$  in brine determined by Thompson-Hamilton<sup>5</sup> for the concentrations and temperatures, shown in Table 18 is plotted in Fig. 42. The curves A and B represent the conductivities

TABLE 18.—SATURATED SOLUTIONS OF  $\text{Cu}_2\text{Cl}_2$  IN BRINE AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Temperature, deg. C.	Saturated solutions of $\text{Cu}_2\text{Cl}_2$ in		
	I 15 g. NaCl in 100 g. $\text{H}_2\text{O}$	II 20 g. NaCl in 100 g. $\text{H}_2\text{O}$	III 30 g. NaCl in 100 g. $\text{H}_2\text{O}$
25	0.145	0.193	0.200
40	0.188	0.245	0.258
50	0.217	0.281	0.298

<sup>1</sup> Kothny, *Oest. Jahrb.*, 1910, LVIII, 141.<sup>2</sup> Truthe, *Zt. anorg. Chem.*, 1912, LXXVI, 161; *Rev. Mét. Extr.*, 1913, X, 379.<sup>3</sup> Cappelen-Smith, 1913.<sup>4</sup> Comey, A. M., "Dictionary of Chemical Solubilities, Inorganic," Macmillan, London, 1896, p. 135.<sup>5</sup> *Tr. Am. Electrochem. Soc.*, 1910, XVII, 287.

of two acid  $\text{CuSO}_4$ -solutions; solution *A* contains 12.5 per cent.  $\text{CuSO}_4 + 5\text{aq}$  and 3.75 per cent. free  $\text{H}_2\text{SO}_4$ , solution *B* 18.3 per cent. salt and 9.2 per cent. free acid.

Solutions of  $\text{Cu}_2\text{Cl}_2$  in brine decompose metallic (Pb, Zn, Cd, Fe, Co, Bi, Sn) sulphides forming their chlorides and  $\text{Cu}_2\text{S}$ . Copper is precipitated from  $\text{Cu}_2\text{Cl}_2$  solutions by Fe; by the electric current ( $\text{Cu}^+ + \text{Cl}^-$ ), when the deposition voltage<sup>1</sup> is 0.731;  $\text{Cu}_2\text{S}$  is precipitated by  $\text{H}_2\text{S}$ , by alkali and alkali earth sulphides;  $\text{Cu}_2(\text{OH})_2$  by  $\text{Ca}(\text{OH})_2$ .

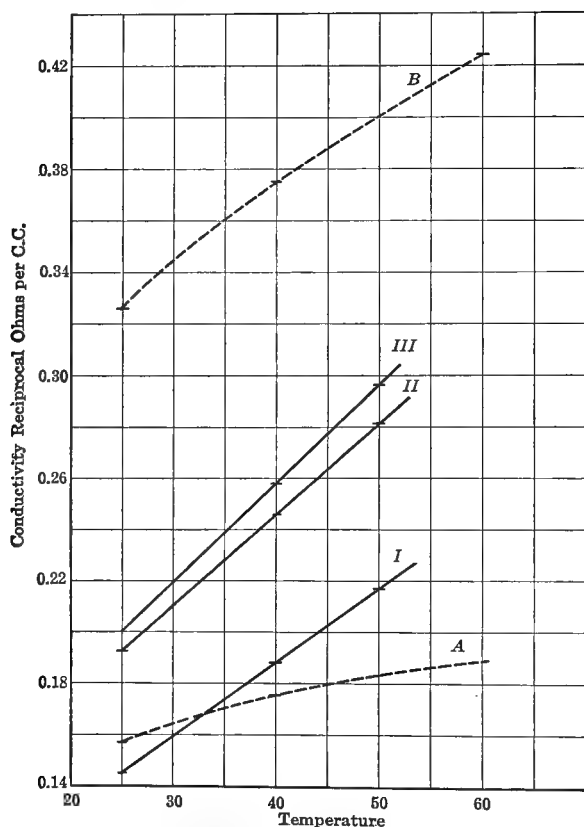


FIG. 42.—Conductivity of  $\text{NaCl}$ -solutions saturated with  $\text{Cu}_2\text{Cl}_2$  (I, II, III), and of  $\text{CuSO}_4\text{-H}_2\text{SO}_4$  solutions (A, B).

**41. Cupric Chloride** ( $\text{CuCl}_2$  47.22 per cent. Cu;  $63.6 \text{ Cu} + 71 \text{ Cl}_2 = 134.6 \text{ CuCl}_2 + 51,400 \text{ cal.}$ , in dil. solution 62,500 cal.), does not occur as a mineral. The anhydrous salt is formed by the action of Cl upon Cu or  $\text{CuCl}$ , of HCl upon powdery  $\text{CuSO}_4$ , and of heat and NaCl upon  $\text{CuSO}_4$ . It is a brown to brownish yellow powder, melts at  $498^\circ \text{C.}$ , is changed at  $340^\circ \text{C.}$  with exclusion of air into  $\text{CuCl} + \text{Cl}$ , with access of air partly into  $\text{CuCl} + \text{Cl}$ , partly into

<sup>1</sup> Abegg, "Handbuch der anorganischen Chemie," pp. 419, 556.

$\text{CuO}$  and  $\text{Cl}$ ;<sup>1</sup> is deliquescent and becomes green. 100 gm.  $\text{H}_2\text{O}$  dissolve at  $0^\circ\text{C}$ .—70.6 g.  $\text{CuCl}_2$ ; at  $17^\circ$ —75.6, at  $31.5^\circ$ —80.8, at  $91^\circ$ —104 g.  $\text{CuCl}_2$ . The hydrous  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  is formed by dissolving  $\text{Cu}$  in *aq. reg.*, or  $\text{CuO}$  in  $\text{HCl}$ , by the reaction  $2\text{NaCl} + \text{CuSO}_4 = \text{Na}_2\text{SO}_4 + \text{CuCl}_2$ ; the salt is light-blue forming a greenish solution when concentrated. The solution has a decomposing effect upon metallic ( $\text{Fe}$ ,  $\text{Co}$ ,  $\text{Zn}$ ,  $\text{Cd}$ ,  $\text{Pb}$ ,<sup>2</sup>  $\text{Ni}$ ,  $\text{Sn}$ ,  $\text{As}$ ,  $\text{Sb}$ ,  $\text{Ag}$ ) sulphides, forming metallic chloride and  $\text{Cu}_2\text{S}$ ; it is reduced to  $\text{CuCl}$  by  $\text{H}_2\text{SO}_3$ , viz.  $2\text{CuCl}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} = \text{Cu}_2\text{Cl}_2 + 2\text{HCl} + 2\text{H}_2\text{SO}_4$  and by boiling with metallic copper,  $\text{CuCl}_2 + \text{Cu} = \text{Cu}_2\text{Cl}_2$ . The metal is precipitated by  $\text{Fe}$ ,  $\text{Hg}$ , and  $\text{Ag}$ , which are converted into chlorides, and by  $\text{FeO}$ , converted into  $\text{Fe}_2\text{O}_3$  and  $\text{FeCl}_2$ ; the sulphide by  $\text{CuS}$  with the separation of  $\text{S}$ , and by  $\text{Ag}_2\text{S}$  with separation of  $\text{S}$  and formation of  $\text{AgCl}$ .  $\text{KOH}$  precipitates  $\text{Cu}(\text{OH})_2$ ;  $\text{H}_2\text{S}$  separates  $\text{Cu}_2\text{S}$  and  $\text{S}$ .

<sup>1</sup> Kothny, *Oest. Jahrb.*, 1910, LVIII, 141.

<sup>2</sup> Hunt, *Tr. A. I. M. E.*, 1881-82, x, 12.

## CHAPTER VI

### COPPER ORES

**42. In General.**—The minerals forming copper ores are quite numerous; they are classed as sulphide, oxide, and native, and form the basis of the classification of copper ores.<sup>1</sup>

**43. Sulphide Copper Ores.**—The sulphide minerals are: Chalcocite (vitreous copper, copper glance),  $\text{Cu}_2\text{S}$ , 79.8 per cent. Cu.; covellite,  $\text{CuS}$ , 66.4 per cent. Cu; bornite (peacock ore),  $3\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$  or  $\text{Cu}_3\text{FeS}_3$ , range 50–70 per cent. Cu, formula: 55.5 Cu, 16.4 Fe, 28.1 S; enargite,  $3\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_5$  or  $\text{Cu}_3\text{AsS}_4$ , 48.3 per cent. Cu, 19.1 As, 32.6 S; chalcopyrite,  $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$  or  $\text{CuFeS}_2$ , 34.5 per cent. Cu, 30.5 Fe, 35.0 S; tetrahedrite (gray copper, fahlore),  $4\text{RS} \cdot \text{Sb}(\text{As})_2\text{S}_3$ ,  $\text{R} = \text{Cu}_2, \text{Fe}, \text{Zn}, \text{Ag}_2, \text{Hg}_2$ , range 15–48 per cent. Cu;  $4\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ , 52.1 per cent. Cu, 24.8 Sb, 23.1 S; tennantite,  $4\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_3$ , 57.5 per cent. Cu, 17.0 As, 25.5 S; chalcantite (blue vitriol),  $\text{CuSO}_4 + 5 \text{ aq}$ ,  $\text{CuO}$  per cent. 31.8,  $\text{SO}_3$  32.1,  $\text{H}_2\text{O}$  36.1; Cu 25.4. To this list must be added pyrite and marcasite,  $\text{FeS}_2$ , 53.4 per cent. S, and pyrrhotite,  $\text{Fe}_n\text{S}_{n+1}$ , range  $\text{Fe}_5\text{S}_6 - \text{Fe}_{16}\text{S}_{17}$ , chiefly  $\text{Fe}_{11}\text{S}_{12}$ , 38.4 per cent. S., both of which are frequently copper-bearing to the extent perhaps of 5 per cent. through intermingled chalcopyrite, or sometimes tetrahedrite. A characteristic metallurgical difference<sup>2</sup> between pyrite and marcasite is that the latter is usually more free-burning and more easily vitriolized than the former.

The leading sulphide copper deposits in the United States are situated in Montana, Utah, Nevada, California, and the Atlantic Coast beds.

The last<sup>3</sup> are massive pyrrhotous deposits, with from 2 to 5 per cent. Cu, occurring in strata extending from Newfoundland to Alabama. The ore is generally first roasted in kilns of sulphuric acid plants before it is treated for copper.

In Montana,<sup>4</sup> in and around Butte, occur rich ores in shattered and altered granite. The copper minerals<sup>5</sup> are chalcocite, bornite, enargite, and pyrite; covellite, tetrahedrite, and chalcopyrite are subordinate. Up to 1900

<sup>1</sup> Weed, W. H., "The Copper Mines of the World," McGraw-Hill Book Co., New York, 1907.

<sup>2</sup> Brown, *Proc. Am. Phil. Soc.*, Philadelphia, 1894, xxxiii, 225; *Zt. prakt. Geol.*, 1895, iii, 180. Stokes, *Bull.* 186, U. S. Geol. Surv., 1901.

<sup>3</sup> Kemp, J. F., "Ore Deposits of the U. S. and Canada," New York, 1900, p. 185. Wilson, W. G., "Pyrites in Canada," Canada Dep't. Mines, Ottawa, 1912.

<sup>4</sup> Weed, H. S., *Profess. Paper*, No. 74, U. S. Geol. Surv., 1912. Sales, *Tr. A. I. M. E.*, 1913, XLVI, 3.

<sup>5</sup> Goodale, *Tr. A. I. M. E.*, 1896, xxvi, 599; Goodale-Klipinger, 1913, XLVI. Bard-Gidel, *op. cit.*, 1913, XLVI, 123.



chalcocite was the leading copper mineral; since then enargite became more prominent. The ore averaged in 1911<sup>1</sup> Cu 3.2, SiO<sub>2</sub> 55, Fe 10 per cent.; 0.0071 oz. Au, 2.20 oz. Ag per ton; there are present 2.3 oz. Te per lb. Cu. The ore is graded as *first class*, about 26 per cent. of the product (with SiO<sub>2</sub> 51.2, Fe 13.6, S 17.3, Al<sub>2</sub>O<sub>3</sub> 8.1, CaO 0.30 per cent. Ag 2.0 and Au 0.015 oz. per ton)<sup>2</sup> which goes straight to the blast-furnace; and *second class*, the remaining 74 per cent. (with SiO<sub>2</sub> 58.5, Fe 9.4, S 11.6, Al<sub>2</sub>O<sub>3</sub> 11.7, CaO 0.10 per cent., Ag 1.26 and Au 0.008 oz. per ton) which goes to concentrating mills furnishing a coarse concentrate (with SiO<sub>2</sub> 20.7, Fe 25.9, S 33.8, Al<sub>2</sub>O<sub>3</sub> 4.4, CaO 0.3 per cent.; Ag 3.9 and Au 0.019 oz. per ton) which goes to the blast-furnaces, and a fine concentrate (with SiO<sub>2</sub> 18.1, Fe 28.5, S 35.9, Al<sub>2</sub>O<sub>3</sub> 5.3, CaO 0.3 per cent., Ag 3.0 and Au 0.021 oz. per ton) which is roasted and then smelted in reverberatory furnaces.

The ores of Bingham, Utah,<sup>3</sup> and Northern Nevada<sup>4</sup> are finely divided chalcocite and chalcopyrite disseminated through porphyry. Utah ores contain about Cu 2.5, Fe 40, SiO<sub>2</sub> 25, CaO 4 per cent., 0.015 oz. Au and 0.15 oz. Ag per ton; Nevada ores 1.2–2 per cent. Cu, 0.01–0.02 oz. Au and 0.3–1 oz. Ag per ton. The ore of the Nevada Consolidated Copper Co. in 1911<sup>5</sup> assayed Cu 1.80 per cent., Au 0.013, and Ag 0.079 oz. per ton. The ores are concentrated to a product assaying about 30 per cent. Cu, 25 Fe, 32 SiO<sub>2</sub>. Similar ores occur in Arizona.

The leading deposits of California are those of Shasta County,<sup>6</sup> where the ore consisting of pyrite with chalcopyrite and benide, averaging 3.77 per cent. Cu and \$1.99 Ag Au, occurs in a granite porphyry. Partial pyritic smelting is practised in the district.

**44. Oxide Ores.**—The oxide minerals are: Cuprite (red oxide of copper), Cu<sub>2</sub>O, 88.8 per cent. Cu; tenorite (melanconite, black oxide of copper), CuO, 79.8 per cent. Cu; malachite, CuCO<sub>3</sub>.Cu(OH)<sub>2</sub>, 57.3 per cent. Cu; azurite, 2CuCO<sub>3</sub>.Cu(OH)<sub>2</sub>, 55.1 per cent. Cu; chrysocolla, CuSiO<sub>3</sub>+2H<sub>2</sub>O, 37.9 per cent. Cu, 34.3 SiO<sub>2</sub>; atacamite, CuCl<sub>2</sub>.3Cu(OH)<sub>2</sub>, 59.4 per cent. Cu, 16.6 Cl; brochantite, CuSO<sub>4</sub>.3Cu(OH)<sub>2</sub>, SO<sub>3</sub> 17.7 per cent., CuO 70.3 (=Cu 56.1), H<sub>2</sub>O 12.0 (Chile). These ores used to occur abundantly in the Southwest,<sup>7</sup> especially in Southeastern Arizona, in limestone and disseminated through eruptive rock. A large part of the ore has changed into sulphide and grown less

<sup>1</sup> *Min. Res.*, U. S. Geol. Survey, 1911, 1, 295.

<sup>2</sup> Goodale, *Tr. A. I. M. E.*, 1913, XLVI.

<sup>3</sup> Boutwell, *Prof. Paper*, U. S. Geol. Surv., 38, 1905.

<sup>4</sup> Lawson, *Bull.* 4, Dep't. Geol. University Cal., p. 284.

<sup>5</sup> *Min. Res.*, U. S. Geol. Survey, 911, 1, 298.

<sup>6</sup> Diller, *Bull.* 213, U. S. Geol. Survey, 1903, pp. 123–132, 1904; pp. 169–179.

Graton, *Bull.* 430, 1910, p. 71.

<sup>7</sup> Wendt, *Tr. A. I. M. E.*, 1886–87, xv, 25.

Ransome, Globe district, *Prof. Paper*, No. 12; U. S. Geol. Surv., 1903.

Ransome, Bisbee district, *Prof. Paper*, No. 21, U. S. Geol. Surv., 1904.

Lindgren, Morenci district, *Prof. Paper*, No. 43, U. S. Geol. Surv., 1905.

Lindgren-Graton, Jerome district, *Bull.* 285, U. S. Geol. Surv. 1906, p. 81.

rich so that in 1908 it averaged 4.36 per cent. Cu. The Bisbee ore averaged in 1911: Cu 5.9 per cent., Au 0.0308 oz. and Ag 1.49 oz. per ton;<sup>1</sup> the Morenci district 3.116 per cent. Cu. Sulphide ore of higher grade, with about 16 per cent. Cu, is smelted raw; that of lower grade, 2+ per cent. Cu, is first concentrated to a product with about 16 per cent. Cu and 30 per cent. SiO<sub>2</sub>; remaining oxide ore is usually smelted with sulphide.

**45. Native Copper** occurs in the Upper Peninsula of Michigan<sup>2</sup> disseminated through amygdaloid and conglomerate beds of eruptive rocks; the rock assays 0.5-1.5 and averages 1.01 per cent. Cu, and is concentrated to 65-85 per cent. Cu and then smelted in reverberatory furnaces. Native copper is very pure<sup>3</sup> containing 99.92 per cent. Cu with small amounts of Ag and Fe, perhaps some traces of Ni and As.

**46. Marketing.**—In marketing copper ores<sup>4</sup> there exist no general standards as is, *e.g.*, the case with Pb and Fe ores, because mine and smeltery usually belong to the same company. Pyritic ores of the Atlantic coast, used for the manufacture of H<sub>2</sub>SO<sub>4</sub>, are rated for the S they contain (not <37 per cent.) in addition to their Cu-contents, and according to size. As regards the latter there are three classes: Lump ore, 8 in. and over; broken, 3 in.— $\frac{3}{4}$  in.; and smalls, under  $\frac{1}{4}$  in.

**47. Metallurgical Treatment in General.**<sup>5</sup>—Copper may be extracted from its ore by pyro-, hydro-, and electro-metallurgical processes. The method chosen will depend upon the character of the copper mineral (sulphide, oxide, native) and the gangue, the copper content of the ore, and the cost of labor, fuel, and material. Smelting is practised with rich and medium-grade ore, because the fuel, the leading expense, increases with the amount of gangue present which has to be converted into slag. Leaching is in place with low grade ore, the gangue of which is not attacked by the solvent, as the amounts of fuel, solvent, and precipitant required are small and the percentage of extraction high; and with intermediary products, such as impure matte or copper containing precious metal. Electrolytic processes have so far been a failure with ore, and a partial success with matte, and have become the standard method for treating metallic copper containing precious metal. The copper obtained by smelting and leaching is impure and has to be fire-refined; that from electrolytic processes is usually too brittle to be used as such, and has to undergo a similar fire-refining process.

<sup>1</sup> *Min. Res.*, U. S. Geol. Survey, 1911, I, 1, 279.

<sup>2</sup> Irving, *Monograph V.*, U. S. Geol. Surv.; *Geol. Survey of Mich.*, vols. v and vi.

<sup>3</sup> T. A. Rickard, "The Copper Mines of Lake Superior," McGraw-Hill Book Co., New York, 1905.

<sup>4</sup> Douglas, *Min. Ind.*, 1894, III, 243.

<sup>5</sup> Barbour, *Eng. Min. J.*, 1911, XCII, 314.

<sup>6</sup> General Review by Kerl, *Berg. Hüttenm. Z.*, 1892, LI, 375;

Review of Recent Progress by Croasdale, *Pac. Coast Miner*, 1903, VII, 471.

## CHAPTER VII

### SMELTING OF COPPER

**48. Smelting of Copper Ore in General.**—The minerals forming copper ores were classed in § 42 under the heads of sulphide, oxide, and native. The smelting of the ore, which is governed by the character of the copper-bearing mineral, differs accordingly; hence the whole subject is best treated under the three heads: Smelting Sulphide-, Smelting Oxide-, and Smelting Native-Copper ores.

#### (A) SMELTING SULPHIDE COPPER ORE

**49. Smelting Sulphide Copper Ore in General.**—Metallurgically considered sulphide copper ores consist mainly of  $\text{CuS}$ ,  $\text{FeS}$ , and gangue, and the aim of smelting is to separate Cu from Fe, S, and gangue. The smelting is based upon the strong affinity of Cu for S<sup>1</sup> and its weak affinity for O in comparison with Fe and the other base metals of the ore, as well as upon the fact that  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{O}$  will react upon one another, giving Cu and  $\text{SO}_2$ .

If an ore rich in S is partially roasted and then subjected to a reducing fusion, be the reducing agent C, CO, or S, the gangue will form a slag. Of the metals, Cu will first unite with the S necessary to form the stable  $\text{Cu}_2\text{S}$ , then the Fe, not taken up by the  $\text{SiO}_2$ , will combine with S to form  $\text{FeS}$ , and subsequently the heavy metals will combine as long as there is S present, in the order of their affinities. The sulphides form a heavy matte which readily separates from the lighter slag, a mixture of silicates of FeO, MnO, CaO, MgO, BaO,  $\text{Al}_2\text{O}_3$  . . . . There exists a variety of roasting apparatus (§ 55). Smelting is carried on in the blast furnace and the reverberatory furnace; electrothermic methods have not passed the laboratory stage.<sup>2</sup>

In blast-furnace smelting the two operations of roasting and smelting may be carried on together by the so-called pyritic process, a fusion in a strongly oxidizing atmosphere. There are two ways of bringing forward to metallic copper the matte produced in ore-smelting.

<sup>1</sup> Hofman, "General Metallurgy," 1913, p. 74, "Sulphides."

<sup>2</sup> Vattier, *Berg. Hüttenm. Z.*, 1903, LXII, 549.

Wolkow, *Metallurgie*, 1910, VII, 99.

Ladd, *Met. Chem. Eng.*, 1910, VIII, 7.

Schilowski, *Metallurgie*, 1910, VII, 99, 151, 435; 1911, VIII, 617; *Eng. Min. J.*, 1912, XCIV, 504.

Stephan, *Metall-Erz.*, 1912-13, X, 11.

Lyon-Keeney, *Tr. A. I. M. E.*, 1913, XLVII, a general review of subject.

(1) By a series of oxidizing roasts, each followed by a reducing fusion, the aim being to expel the electro-negative components of the matte (S, As, Sb), and to slag the electropositive in the order of their affinities for O, until copper is finally obtained in the metallic state. The roasts are carried on in suitable apparatus, and the fusions sometimes in blast furnaces, but more commonly in reverberatory furnaces.

(2) By converting, *i.e.*, forcing compressed air through molten matte held, at the right temperature, in a suitable vessel whereby oxidation by O and reduction by S go on simultaneously until  $\text{Cu}_2\text{S}$  and an iron slag is obtained, when, after pouring off the slag, the remaining S is expelled and metallic copper obtained. Low-grade matte is frequently brought forward to converting grade by partial pyritic smelting in the blast furnace. Most of the smelteries of the United States are situated far enough away from populous centers or agricultural regions to make it possible to allow the sulphurous converter gases to pass off into the open, but in Europe this is not the case; hence converting is the predominant process in the United States for extracting Cu from matte, in Europe it is the exception.

The outline shows that several operations are necessary for the extraction of Cu from sulphide ore by smelting. The recovery cannot be accomplished by a dead-roast followed by a single fusion, as it would be difficult to collect all the reduced Cu, especially in case of low-grade ores, and as the recovered Cu would be very impure, containing excessive amounts of Fe, beside much As and Sb.

**50. Smelting Sulphide Copper Ore in the Blast Furnace in General.**—Three processes have to be distinguished, all of which aim to produce matte and slag.

(1) THE ROASTING AND REDUCTION PROCESS, also called *German* or *Swedish* process. The raw ore is subjected to an oxidizing roast, and the partially roasted ore smelted in the blast furnace with much carbonized fuel or anthracite to furnish the necessary heat and reducing agent.

(2) THE PYRITIC PROCESS, also called *American* process. The raw ore is smelted in the blast furnace without carbonaceous fuel in an oxidizing atmosphere, the oxidation of Fe and S, and the slag formation, furnishing the necessary heat.

(3) THE PARTIAL PYRITIC PROCESS, a modification of (2), in which a lack of heat is made up by charging a small amount of fuel with the ore.

The roasting and reduction process, the oldest of the three, is being replaced by the pyritic processes whenever the character of the ore makes this possible. The requirements that an ore has to fulfil to permit pyritic smelting are so strict that smelting without any fuel whatever is the exception, but partial pyritic smelting, in the United States at least, is becoming more and more common. The pyritic processes will be discussed together after the roasting and reduction process.

**51. The Roasting and Reduction Process.**—The operations to be considered are roasting of raw ore, smelting of roasted ore in the blast-furnace for matte and slag, roasting of matte, smelting of roasted matte in the blast-furnace for impure, so-called black, copper, and slag.

## I. ROASTING

**52. Roasting Sulphide Copper Ore.**—The object of roasting is to oxidize S and Fe, and to remove volatile impurities such as As, Sb, and Bi. The degree to which a roast is to be carried depends upon the percentages of S, Cu, and Fe, and the amount of impurity present. An ore rich in Cu will require less roasting than one that is poor for the production of matte with a given copper content. As regards impurities, the larger the amount of S present, and the slower and more prolonged the roast, the greater will be their elimination. Thus Gibb<sup>1</sup> found that in a cuprous pyrite with Cu 5.55, As 1.18, Sb 0.035, Bi 0.011 per cent., roasted in a heap, there was eliminated As 75.1, Sb 25.4, Bi 27.8 per cent.; Wendt<sup>2</sup> roasting a similar ore with Cu 5.15, As 1.30, Sb 1.45, S 32.35, Fe 29.36 per cent., in a kiln,<sup>3</sup> the roasted ore having lost about 20 per cent. in weight, gave the following losses, As 97, Sb 86, S 72 per cent. In roasting a concentrate of chalcopyrite and pyrite with some bornite and chalcocite in a reverberatory furnace, Gibb<sup>4</sup> found the expulsions to be As 61.2, Sb 18.8, Bi 11.3 per cent. In special cases, the roast may be purposely carried so far that in the subsequent reducing fusion there will not be enough S present to cover all the Cu, with the result that there will be formed some metallic copper which will carry down with it impurities, such as As, Sb, Bi, etc., to be refined by special processes, and a matte correspondingly cleaned. The general discussion of the behavior of metallic sulphides in an oxidizing roast, both in powder and lump form, is given elsewhere.<sup>5</sup>

**53. Behavior of Cu-, Fe-, and Mn-sulphides in Powder Form.** (1)  $\text{Cu}_2\text{S}$ , CHALCOCITE.—The changes chalcocite undergoes in an oxidizing roast are generally stated to be as follows:  $\text{Cu}_2\text{S} + 3\text{O} = \text{Cu}_2\text{O} + \text{SO}_2$ ,  $\text{Cu}_2\text{O} + \text{SO}_2 + \text{O} = \text{CuO} + \text{SO}_3$ ,  $\text{CuO} + \text{SO}_3 \rightleftharpoons \text{CuSO}_4$ . Aubell's<sup>6</sup> laboratory experiments with prepared finely divided  $\text{Cu}_2\text{S}$  show that roasting starts at 200° C with the reaction  $2\text{Cu}_2\text{S} + 5\text{O}_2 = 2\text{CuO} + 2\text{CuSO}_4$ , and continues up to 330°; above this temperature the reaction  $\text{Cu}_2\text{S} + \text{O}_2 = 2\text{CuO} + \text{SO}_2$  begins; up to 550° more than half of the sulphide-S is converted into sulphate-S. The  $\text{SO}_3$ , formed by the dissociation of  $\text{CuSO}_4$ , acts oxidizingly,  $\text{Cu}_2\text{S} + 3\text{SO}_3 = \text{Cu}_2\text{O} + 4\text{SO}_2$  and  $\text{Cu}_2\text{O} + \text{SO}_3 = 2\text{CuO} + \text{SO}_2$ . As long as the roasting ore contains  $\text{Cu}_2\text{S}$ , there will be formed  $\text{Cu}_2\text{O}$ , so that after all the S has been expelled, the roasted ore may retain as much as 30 per cent.  $\text{Cu}_2\text{O}$ , which has to be converted into CuO by air at a temperature below 1069° C.

Chalcocite<sup>7</sup> ignites in air in the range of 430 and 697° C. according to the size of grain, 0.1–>0.2 mm.; it does not decrepitate. That  $\text{Cu}_2\text{S}$  shows a

<sup>1</sup> *Tr. A. I. M. E.*, 1903, XXXIII, 654.

<sup>2</sup> *Op. cit.*, 1890–91, XIX, 100.

<sup>3</sup> Gmehling, *Oest. Zt. Berg. Hüttenw.*, 1890, XXXVIII, 272, details and drawings.

<sup>4</sup> *Loc. cit.*

<sup>5</sup> Hofman, "General Metallurgy," 1913, p. 403.

<sup>6</sup> *Oest. Jahrb.*, 1910, LVIII, 131.

<sup>7</sup> Friedrich, *Metallurgie*, 1909, VI, 1691.

tendency to sinter while roasting, as stated by Plattner,<sup>1</sup> cannot be due to the fusion of  $\text{Cu}_2\text{S}$ , as its melting point lies at  $1127\text{--}1130^\circ\text{C}$ .; the sintering he did observe must have been due to some other cause, perhaps the formation of an oxysulphide. In a laboratory sulphatizing roast carried on between  $420$  and  $440^\circ\text{C}$ ., Warlimont<sup>2</sup> succeeded in rendering 52.5 per cent. of the Cu water-soluble.

(2)  $\text{CuS}$ , COVELLITE.—As  $\text{CuS}$  gives up one molecule of S when brought to a bright red with exclusion of air, and is converted into  $\text{Cu}_2\text{S}$ , its behavior in roasting should be similar to that of  $\text{Cu}_2\text{S}$ .

(3)  $\text{FeS}$ , PYRRHOTITE,  $\text{Fe}_{11}\text{S}_{12}$ .—The changes  $\text{FeS}$  undergoes may be expressed according to Plattner's outline by  $\text{FeS} + 3\text{O} = \text{FeO} + \text{SO}_2$ ,  $3\text{FeO} + \text{O} = \text{Fe}_3\text{O}_4$ , and  $\text{SO}_2 + \text{O} + \text{catalyzer} = \text{SO}_3$ ;  $2\text{Fe}_3\text{O}_4 + \text{SO}_3 = 3\text{Fe}_2\text{O}_3 + \text{SO}_2$  and  $\text{FeO} + \text{SO}_3 = \text{FeSO}_4$ ;  $2\text{FeSO}_4 + \text{heat} = \text{Fe}_2\text{SO}_6 + \text{SO}_2$  and  $\text{Fe}_2\text{SO}_6 + \text{heat} = \text{Fe}_2\text{O}_3 + \text{SO}_3$ . According to Kothny,<sup>3</sup> heating  $\text{FeSO}_4$  in a current of  $\text{CO}_2$  at  $280^\circ\text{C}$ . causes it to be converted into  $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 + \text{SO}_2$  up to  $530^\circ\text{C}$ ., when the basic ferric sulphate is dissociated into  $\text{Fe}_2\text{O}_3$  and  $\text{SO}_3$ . Heating in a current of air gives rise to the reaction  $4\text{FeSO}_4 + \text{O}_2 = 2(\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3)$  within a temperature range of  $150$  and  $380^\circ\text{C}$ . Between  $380$  and  $530^\circ$  some  $\text{SO}_2$  is set free; above  $530^\circ$  decomposition again sets in. The oxidation of  $\text{FeS}$  may progress more directly than shown above, as seen by the equations  $4\text{FeS} + 7\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 4\text{SO}_2$  and  $\text{FeS} + 2\text{O}_2 = \text{FeSO}_4$ . In roasting there has to be considered also the oxidation of  $\text{FeS}$  by  $3\text{SO}_3$  to  $\text{FeO}$  and  $4\text{SO}_2$ . Pure  $\text{FeS}$  ignites in air at from  $325^\circ$  (0.1 mm.-grain) to  $472^\circ\text{C}$  ( $>0.2$ -mm. grain), pyrrhotite at from  $430$  to  $590^\circ$ . The former does not decrepitate; the latter does somewhat.<sup>4</sup> Kothny<sup>5</sup> found that finely divided prepared  $\text{FeS}$  begins to oxidize to  $\text{FeSO}_4$  at  $170^\circ\text{C}$ ., continues to do this up to  $430^\circ$ , when mainly  $\text{Fe}_2\text{O}_3$  and  $\text{SO}_2$  are formed accompanied by some  $\text{FeSO}_4$ . In fact the presence of  $\text{FeSO}_4$  is noticeable up to  $600^\circ\text{C}$ . In a laboratory sulphatizing roast, Warlimont<sup>6</sup> rendered in 5 hr. 31.8 per cent. of the Fe water-soluble.

(4)  $\text{Cu}_2\text{S}$ ,  $\text{Fe}_2\text{S}_3$ , CHALCOPYRITE.—The general behavior is similar to that of pyrrhotite except that beside  $\text{Fe}_x\text{O}_y$  and  $\text{FeSO}_4$  there is formed  $\text{Cu}_x\text{O}_y$  and  $\text{CuSO}_4$ ; the formation of water-soluble  $\text{CuSO}_4$  is greatly assisted by the presence of  $\text{Fe}_x\text{S}$ . Thus Warlimont<sup>7</sup> succeeded in rendering 97.7 per cent. Cu water-soluble with a mixture of  $1\text{Cu}_2\text{S} : 10\text{FeS}$ . Similar extractions were obtained by Wedge.<sup>8</sup> Chalcopyrite decrepitates upon heating.

(5)  $\text{FeS}_2$ , PYRITE.—If heated to  $700^\circ\text{C}$ . with exclusion of air the reaction  $\text{FeS}_2 + \text{heat} = \text{FeS} + \text{S}$  takes place, the product resembling the magnetic

<sup>1</sup> "Röstprocesse," p. 79.

<sup>2</sup> *Metallurgie*, 1909, VI, 132.

<sup>3</sup> *Oest. Jahrb.*, 1910, LVIII, 112; *Metallurgie*, 1911, VIII, 389.

<sup>4</sup> Friedrich, *loc. cit.*

<sup>5</sup> *Loc. cit.*

<sup>6</sup> *Loc. cit.*

<sup>7</sup> *Loc. cit.*

<sup>8</sup> *Eighth Internat. Congress of Appl. Chem.*, 1912, III, 151; *Tr. A. I. M. E.*, 1912, XLIV, 818, in large-scale work with his roasting kiln (§§ 69, 214).

sulphide;<sup>1</sup> however, the expulsion of S begins at 200°.<sup>2</sup> According to Friedrich,<sup>3</sup> pyrite from Elba heated in air gives off SO<sub>2</sub> at 405° C. and glows at 533° C.; the more free-burning mineral from Rio Tinto begins to roast at from 260 to 275° C.<sup>4</sup> Kothny's<sup>5</sup> experiments show that 250° C. is the lowest roasting temperature. Pyrite from some localities decrepitates readily; from others it does not; the latter brings a higher price. FeS<sub>2</sub> is more readily roasted than FeS, as the expulsion of S by distillation makes the mineral porous, and as the larger amount of SO<sub>3</sub> formed exerts its strongly oxidizing influence. Assuming that no S is distilled, the complete oxidation of FeS<sub>2</sub>, as formulated by Waring,<sup>6</sup> is expressed by  $4\text{FeS}_2 + 11\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$ ; the formation of Fe<sub>3</sub>O<sub>4</sub> with a short supply of air, by  $\text{FeS}_2 + \text{O}_2 = \text{FeS} + \text{SO}_2$  and  $\text{FeS} + 10\text{Fe}_2\text{O}_3 = 7\text{Fe}_3\text{O}_4 + \text{SO}_2$ . The experiments of Kothny<sup>7</sup> have shown that between 250 and 290° C. the oxidation of FeS<sub>2</sub> takes place according to  $\text{FeS}_2 + 3\text{O}_2 = \text{FeSO}_4 + \text{SO}_2$ , and between 290 and 500° C. according to  $4\text{FeS}_2 + 11\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$  when the FeS<sub>2</sub> kindles. Oxidation to FeSO<sub>4</sub> is, however, noticeable up to 600° C. He also showed that the reactions  $\text{FeS}_2 + 5\text{Fe}_2\text{O}_3 = 11\text{FeO} + 2\text{SO}_2$  and  $\text{FeS}_2 + 16\text{Fe}_2\text{O}_3 = 11\text{Fe}_3\text{O}_4 + 2\text{SO}_2$  do occur, beginning at 380° C. and requiring that for 1 molecule FeS<sub>2</sub> there be present 16 mol. Fe<sub>2</sub>O<sub>3</sub>.

(6) MNS, ALABANDITE.—This compound, which melts at 1162° C.,<sup>8</sup> is converted by roasting into MnSO<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub>. The MnSO<sub>4</sub> begins to give off SO<sub>3</sub> at 699° C.; the dissociation<sup>9</sup> into Mn<sub>3</sub>O<sub>4</sub>, SO<sub>3</sub>, SO<sub>2</sub>, and O is energetic at 790°. Friedrich<sup>10</sup> found that alabandite with 2.02 and 1.98 per cent. Fe, when 0.1 mm. fine, ignited at 355° C.; when coarser than 0.2 mm., at 700° C.; the mineral did not decrepitate.

**54. Behavior of Fe-, Cu-, and Mn-sulphides in Lump Form. KERNEL ROASTING.**—In roasting a sulphide copper ore or matte in lump form, the oxidation will start at the surface of a lump, when this has been brought to the kindling temperature, and then penetrate toward the center at a speed governed by the heat evolved, which causes the lump to swell, become porous, and crack, and thus furnish channels for the travel of the air. In time the surface will become covered with a rind or shell of more or less porous Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>, through which finally the air cannot penetrate sufficiently to complete the oxidation. This is effected by SO<sub>3</sub>, viz.,  $\text{SO}_3 + \text{Met. S} = \text{SO}_2 + \text{Met.O}$ ; but part of the SO<sub>2</sub>

<sup>1</sup> Valentine, *Tr. A. I. M. E.*, 1889-90, XVIII, 78.

Geodel, *J. für Gasbeleuchtung*, 1905, XLVIII, 400.

Friedrich, *Stahl u. Eisen*, 1911, XXXI, 2040.

Barth, *Metallurgie*, 1912, IX, 204 (600° C.).

<sup>2</sup> Kothny, *loc. cit.*

Barth, *loc. cit.*, 350° C.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> Chalon, *Rev. Un. Min.*, 1902, LVII, 201.

<sup>5</sup> *Loc. cit.*

<sup>6</sup> *Min. Mag.*, 1905, XII, 196.

<sup>7</sup> *Loc. cit.*

<sup>8</sup> Fay, *Proc. Am. Soc. Test. Mat.*, 1908, VIII, 92.

<sup>9</sup> Hofman-Wanjukow, *Tr. A. I. M. E.*, 1912, XLIII, 548.

<sup>10</sup> *Metallurgie*, 1910, VII, 329.

is decomposed,  $3\text{SO}_2 = \text{S} + 2\text{SO}_3$ , setting free S-vapor, which, traveling toward the cooler center of a lump, is likely to cause the formation of a kernel of sulphide. If the ore is low in Cu, the S in a roasted lump may have been almost completely expelled, and the Cu converted into  $\text{CuO}$ , only a small part retaining the transitional forms of  $\text{Cu}_2\text{O}$  and  $\text{CuSO}_4$ . If the ore is rich in Cu, the roasted lump may contain some metallic Cu formed by  $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} = 6\text{Cu} + \text{SO}_2$  and by  $3\text{Cu}_2\text{O} + \text{FeS} = 6\text{Cu} + \text{FeO} + \text{SO}_2$ . If the ore contains some  $\text{Ag}_2\text{S}$ , the silver in the roasted lump will be present as  $\text{Ag}_2\text{SO}_4$  or Ag, the latter having been formed by  $\text{Ag}_2\text{S} + 2\text{O} = 2\text{Ag} + \text{SO}_2$  or by  $\text{Ag}_2\text{SO}_4 + \text{Ag}_2\text{S} = 4\text{Ag} + 2\text{SO}_2$ ,<sup>1</sup> and not by decomposition of  $\text{Ag}_2\text{SO}_4$ , which takes place at  $925^\circ \text{C}$ .<sup>2</sup>

A special form of roasting copper ore in lump form is *Kernel Roasting*,<sup>3</sup> whereby the small quantity of Cu in a low-grade pyritic ore is concentrated in the center of the lump as a kernel of sulphide, which thus becomes rich, while the surrounding shell or rind, converted into a mixture of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ , is correspondingly impoverished, retaining small quantities of copper as  $\text{CuSO}_4$  and  $\text{Cu}_2\text{O}$ . Edward<sup>4</sup> has noted an enrichment of the rind in Ag; a similar phenomenon was observed by Plattner<sup>5</sup> with matte whether lead-bearing or not.

Figs. 43-45 show three characteristic stages in heap- or stall-roasted copper-bearing pyritic ore of suitable size and character. Lürzer<sup>6</sup> shows a very high degree of concentration in the following analyses:

Crude ore, Cu 1.60, Fe 43.50, S 50.25,  $\text{SiO}_2$  5.00 per cent.

Pure kernel, Cu 41.64, Fe 28.76, S 29.28,  $\text{SiO}_2$  0.08 per cent.

Rind next to kernel, Cu 3.31, S 0.92,  $\text{SiO}_2$  2.85,  $\text{CuO}$  1.58, Fe 0.10,  $\text{Fe}_2\text{O}_3$  85.70,  $\text{SO}_3$  2.50, ignition loss 3.04 per cent.

Concentration<sup>7</sup> of ore with 3-4 per cent. Cu into kernels with 15-20 per cent. Cu and rinds with 2 per cent. Cu was common at Fahlun. At Agordo,<sup>8</sup> ore with 2 per cent. Cu gave 13 per cent. kernels with 6 per cent. Cu, and 87 per cent. rinds with 1.28 per cent. Cu (calculated). Schnabel<sup>9</sup> gives from his work in the Caucasus a concentration of Cu, from ore with 7-10 per cent. Cu, into kernels with 35-40 per cent. Cu, the rinds assaying 3 to 4 per cent. Cu, of which  $2\frac{1}{2}$  to 3 parts were  $\text{CuSO}_4$  and  $\frac{1}{2}$  to 1 part  $\text{CuO}$ . This concentration of Cu toward the center has been attributed by Plattner<sup>10</sup> to  $\text{Cu}_2\text{S}$  becoming liquefied and being drawn toward the center. Now  $\text{Cu}_2\text{S}$  melts at  $1127-1130^\circ \text{C}$ ., a temperature not reached in a heap- or stall-roast. Schertel<sup>11</sup> thinks it a process of adhesion and not one of fusion. Considering that the kernel at the end of the roast is a

<sup>1</sup> Sackur, *Ber. deutsch. chem. Ges.*, 1908, XLI, 3356.

<sup>2</sup> Hofman-Wanjukow, *loc. cit.*

<sup>3</sup> Peters, *Min. Res. U. S. Geol. Surv.*, 1882, p. 287.

<sup>4</sup> *Eng. Min. J.*, 1895, LIX, 411.

<sup>5</sup> "Röstprocesse," pp. 183, 205.

<sup>6</sup> *Tunner's Jahrb.*, 1853, III, 339.

<sup>7</sup> Bredberg, *Erdmann's J. Technisch-Oekonomische Chem.*, 1829, IV, 300.

<sup>8</sup> Egleston, *Sch. Min. Quart.*, 1887-88, IX, 124.

<sup>9</sup> Schnabel-Louis, *Handbook of Metallurgy*, 1905, I, 39.

<sup>10</sup> "Röstprocesse," p. 195.

<sup>11</sup> *Dingl Polyt. J.*, 1872, CCVI, 284.



- a.* Crust of ferric oxide.
- b.* Layer of enriched sulphide (chalcopyrite).
- c.* Unaltered center.

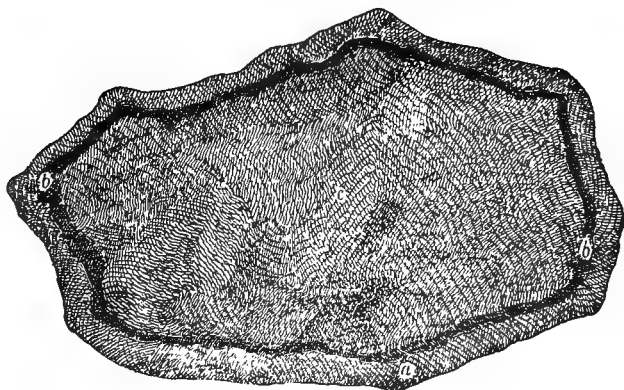


FIG. 43.—Roasted for a short time.

- a.* Crust of ferric oxide.
- b.* Layer of enriched sulphide (bornite).
- c.* Layer of enriched sulphide (bornite).
- d.* Layer of enriched sulphide (chalcopyrite).
- e.* Unaltered center.

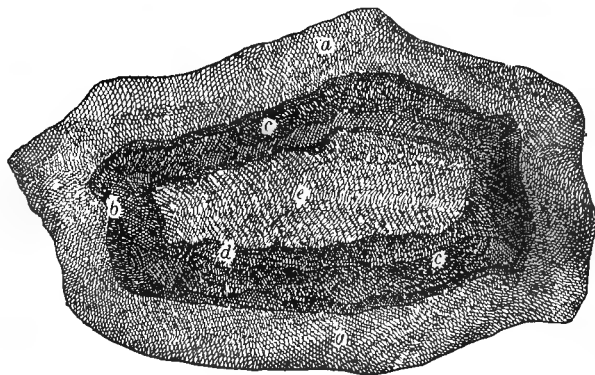


FIG. 44.—Roasted for a longer time.

- a.* Crust of ferric oxide usually much cracked.
- b.* Kernel of enriched sulphide.

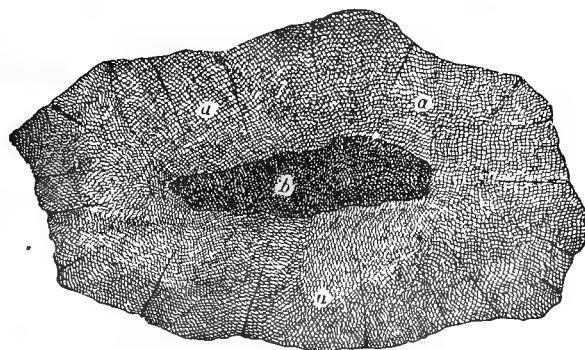


FIG. 45.—Final stage of roast.

FIGS. 43-45.—Three stages in kernel-roast of pyritic copper ore (Plattner).

mixture of  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ , it may be that instead of  $\text{Cu}_2\text{S}$ , the eutectic (see matte § 119) of the two components, which melts below  $950^\circ \text{C}$ ., travels inward. Another theory is that of Poole,<sup>1</sup> who states that S, which thickens when heated for some time to above its melting point, forms a very thin liquid when finely divided.  $\text{Cu}_2\text{S}$  or  $\text{FeS}$  is stirred into it, and suggests that this thin liquid travels toward the center. The latest theory is one by Friedrich,<sup>2</sup> who bases it on the experimental fact observed by Schenck-Hempelmann<sup>3</sup> that heating a mixture of  $\text{CuSO}_4$  and  $\text{Cu}_2\text{S}$  to a temperature lying between 300 and  $400^\circ \text{C}$ . causes the formation of a viscous brownish fluid. He believes that the essential point in the fusion of  $\text{Cu}_2\text{S}$  at a very low temperature, is satisfactorily explained.

Presupposing the existence of a plastic or fluid substance, there remain to be given an explanation of the cause for the inward travel from the bottom upward and from the side inward. Howe<sup>4</sup> suggests capillary attraction which causes the plastic part to adhere to the solid; McCross<sup>5</sup> and Austin<sup>6</sup> suggest magnetic attraction on account of the plastic mass becoming not only magnetizable, but magnetic; Knapp<sup>7</sup> and Roberts-Austen<sup>8</sup> suggest diffusion which might be active without any fusion whatever. There is no reason why the three forces should not supplement one another. The suggestions of H.G.Z.<sup>9</sup> of an outward movement of  $\text{FeS}$ , and of Edwards<sup>10</sup> of an inward movement of  $\text{CuO}$  do not appear reasonable.

A successful kernel-roast<sup>11</sup> requires a copper-bearing pyrite of say 4 in. in diameter that does not decrepitate upon heating and is nearly free from gangue and a slow roast at a regulated low temperature. It is carried on in heaps and stalls. The oxidation of a lump begins at the surface, the heat generated sublimes some of the S which protects  $\text{Cu}_2\text{S}$  from oxidation; the  $\text{Cu}_2\text{S}$  alone or with some  $\text{FeS}$  travels inward while the excess  $\text{FeS}$  is oxidized by the action of air or  $\text{SO}_3$ . In ordinary heap- or stall-roasts, the limiting size for lump-ore is a 3-in. ring, as with larger pieces there is a tendency to the formation of kernels a condition which is usually avoided as much as possible.

**55. Roasting Apparatus in General.**—The roasting of copper ores is carried on in heaps, stalls, shaft-, reverberatory-, and muffle-furnaces, and in blast roasting apparatus. The roaster gases from heaps, stalls, and reverberatory furnaces contain under 1 per cent.  $\text{SO}_2$  and are contaminated with fuel gases hence they cannot be economically utilized.<sup>12</sup> Those from shaft- and muffle

<sup>1</sup> *Tr. A. I. M. E.*, 1906, XXXVI, 403.

<sup>2</sup> *Metall-Erz*, 1914, XI, 9.

<sup>3</sup> *Op. cit.*, 1913, X, 293.

<sup>4</sup> *Eng. Min. J.*, 1895, LIX, 104, 267, 364.

<sup>5</sup> *Op. cit.*, pp. 195, 339.

<sup>6</sup> *Min. and Meth.*, 1911, II, 119.

<sup>7</sup> *Eng. Min. J.*, 1895, LIX, 339.

<sup>8</sup> "Introduction to the Study of Metallurgy," 1910, 55.

<sup>9</sup> *Eng. Min. J.*, 1895, LIX, 147.

<sup>10</sup> *Op. cit.*, p. 411.

<sup>11</sup> Howe, *op. cit.*, 1895, LIX, 104-267.

<sup>12</sup> Hofman, "General Metallurgy," 1908, p. 88.

furnaces contain over 4 per cent.  $\text{SO}_2$ <sup>1</sup> and are free from fuel-gases; they can be converted into  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$  or  $\text{SO}_3$ . The  $\text{SO}_2$ -content from intermittent blast-roasting apparatus varies considerably; usually the gases go to waste; in some instances several pots are run in series in such a manner as to furnish a roaster-gas of uniform grade with over 4 per cent.  $\text{SO}_2$ . From the continuous blast roaster of von Schlippenbach<sup>2</sup> the sulphurous gas is utilized in the manufacture of  $\text{H}_2\text{SO}_4$ .

The choice of furnace is governed by the chemical composition (mainly percentage of S and Fe), physical character (coarse or fine), and the value of the ore (percentage of Cu, Ag, Au), or the time that can be given to the roasting. It is further influenced by the degree of desulphurization that is demanded, by the practicability of recovering the sulphurous gases or the necessity of rendering them harmless, and lastly by the price of labor, fuel, and material.

**56. Roasting in Heaps.**<sup>3</sup>—Since the advent of partial pyritic smelting, this method of roasting has lost much of its former importance. It is suited for coarse ore with an admixture of only a small amount of fines; and consists, Figs. 46–48, in piling the ore to the form of a truncated pyramid on to a bed of wood on suitable ground, and igniting the fuel, which heats the superincumbent ore and starts the roasting. If the ore contains sufficient S to keep up combustion, the process of roasting will proceed of its own accord; if not, the lack has to be made up by mixing in fuel (coke or coal fines, refuse wood, etc.). Ores containing less than 15 per cent. S require intermixing of fuel.

(1) **THE ROAST-YARD.**—The location of the roast-yard has to be so chosen that the heaps are protected from strong winds, and that the prevailing wind carries the gases away from the works. Ore-heaps are rarely covered by sheds as is often the case with the more valuable matte-heaps. In order to have a cheap roast it is essential that there be as little handling as possible of raw and roasted ore; special provision has to be made for this.

One of the simplest arrangements of roast-yard is that formerly in operation at the Vershire copper mines, near Corinth, Vt., shown in Figs. 49–51. The ore is brought in side-dump cars on a trestle at an elevation of from 10 to 12 ft. across the places where the heaps are to be erected; the trestle carries T-rails and has a slight grade, from  $\frac{3}{4}$  to 1 per cent. Parallel with the upper track and about 4 ft. below the level of the yard is a second track over which the roasted ore is run to the feed floor of the blast-furnace, the tops of the cars being on a level with the floor of the yard. Similar permanent plants are those

<sup>1</sup> Hofman, *op. cit.*, p. 881.

<sup>2</sup> Hofman, *Min. Ind.*, 1910, XLI, 761.

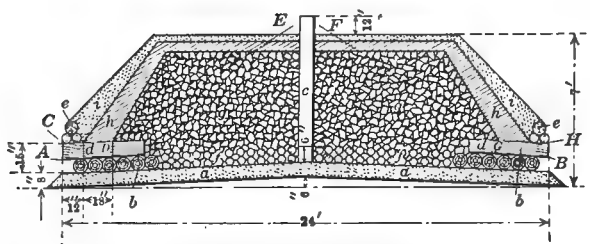
Kroupa, *Oest. Zt. Berg. Hüttenw.*, 1912, XL, 539.

<sup>3</sup> Peters, *Min. Res.*, U. S. Geol. Surv., 1882, 283; 1883–84, 283; "Modern Copper Smelting," New York, 1895, p. 104.

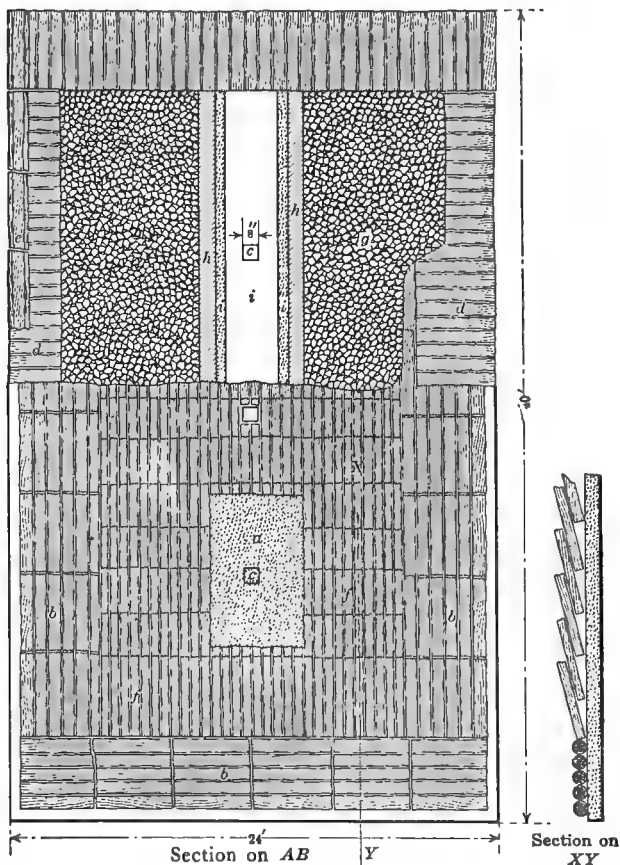
Glenn, *Eng. Min. J.*, 1883, XXXVI, 392.

Wendt, *Sch. Min. Quart.*, 1885–86, VII, 154, 281, 301.

Cross Section



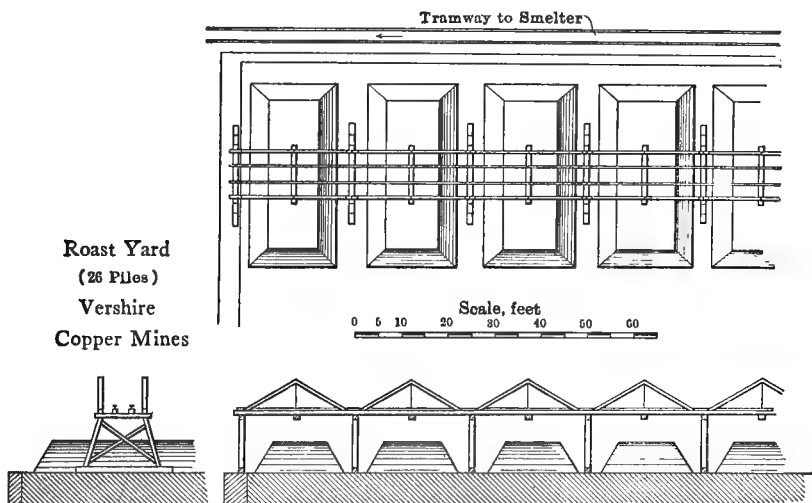
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FIGS. 46-48.—Roast-heap.

given by Peters,<sup>1</sup> and the more complicated arrangement of the Tye Copper Co., Ladysmith, B. C., with Kiddie movable bridges.<sup>2</sup>

At Keswick, Cal.,<sup>3</sup> the ore was delivered in 10- to 20-ton cars to bunkers of 150 tons capacity closed with grizzlies (3-in. slots); beneath was another set of screens with 1- to  $\frac{3}{4}$ -in. holes, thus furnishing coarse, medium, and fine ore, which dropped into separate cars of 2500 lb. capacity. The cars, with 18-in. gauge, were run on 16-lb. rails, which were spiked to 4×4-in. ties laid across 6×8-in. stringers, 16 ft. long, connecting the bents 10 to 12 ft. above the roast-yard.



FIGS. 49-51.

The bents of a trestle were made of round poles, 4-6 in. in diameter at the small ends. When a heap was erected, the rails, stringers, and ties were removed to be used in another heap, while the poles were left in place, the cost of extracting them being greater than their value.

At the works of the Canadian Copper Co., Copper Cliff, Ont., the roast-yard has a capacity of 100,000 tons. In building a heap, the ore is wheeled from a flat car and spread, the base of the heap being 1-2 ft. distant from the track. The roasted ore is loaded from either side of the heap by means of a steam-shovel, having a bucket of 2.5 tons capacity, on to 50-ton ore cars; it takes about 5 min. to load a car. When the ore is badly sintered, 40-per cent. dynamite is used to loosen the material.

The roast-heaps of the Tennessee copper were arranged similarly to those at Copper Cliff, only they were smaller.

<sup>1</sup> "Copper Smelting," p. 111.

<sup>2</sup> *Rep.* to Minister of Mines, Brit. Columbia, 1902, p. 243.

Brewer, *Min. Sc. Press*, 1903, LXXXVII, 7; *Eng. Mag.*, 1904-05, XXVIII, 348.

Jacobs, *Eng. Min. J.*, 1904, LXXVIII, 748.

<sup>3</sup> Neilson, *op. cit.*, 1899, LXVIII, 457.

At the works of the Mond Nickel Co., Victoria Mines, Ont., the roast-yard is situated half way between the mine and the smelter, which are two miles apart. The ore is crushed at the mine and passed over a  $\frac{3}{4}$ -in. screen; it is then transported by a Bleichert elevated tramway to the roast-yard, and the roasted ore by the same means to the blast-furnaces. The train handles in 10 hr. 400 tons of ore in buckets holding 800-900 lb.; there are 180 cars on the two lines, which travel at a speed of 3.5 miles per hour. The tension station is at the roast-yard. Here the buckets are unloaded into small ore-cars and the contents distributed on to the heaps over temporary trestles. The roasted ore is shoveled into 2-ton cars; these are hauled by horses to the base of incline, raised by a gasoline hoist, and discharged into bins, the contents of which are drawn into the Bleichert buckets and carried to the feed floor of the blast-furnaces.

At the new plant of the company at Coniston, Ont., the ore is discharged from bottom side-dump cars into ditches running longitudinally between the roast-heaps, which are placed end to end. Grab-bucket cranes on standard-gauge tracks pick up the ore from the ditches and drop it on the beds. The same cranes excavate and load the roasted ore into 50-ton steel dump cars, which are hauled to the smelter bins. The grab-buckets are designed for digging up ore that is more or less sintered.

(2) THE AREA of roast-yard necessary for furnishing daily a given amount of ore is very large. A heap  $40 \times 24$  ft. and 6 ft. high, holds 240 tons ore and burns 70 days; adding 10 days for building and removing makes 80 days. Such a heap then furnishes per day 3 tons of roasted ore; 35 heaps give 105 or in round figures 100 tons ore per day. Allowing 10 ft. at the ends and 6 ft. at the sides of a heap for working, gives an area of  $60 \times 36 = 2160$  sq. ft. for a heap, or 75,600 sq. ft. for 35 heaps or 100 tons roasted ore per day.

(3) THE GROUND on which heaps are to be built ought to be dry and hard, similar to a macadamized road. A ditch dug at the upper end prevents water from entering the yard which slopes either toward the lower end or the two sides. Drainage may be assisted by underground drain pipes. At Ducktown, Tenn.,<sup>1</sup> 31.4 per cent. of the Cu in a heap was lost by defective drainage, being leached by frequent heavy rains. If the ground is soft, it becomes mixed with the roasted ore;<sup>2</sup> it may be hardened by removing the surface with a scraper, filling the excavated space with rock or coarse slag, and the interstices between the latter with gravel, concentrator-tailing, or granulated slag, and covering the new surface with loam and rolling it down. The finished yard should be two or more inches higher than the surroundings.

(4) CRUSHING AND SIZING OF ORE.—The most suitable size of ore for roasting is from 1.75 to 2 in. if it contains under 25 per cent. S, and 3 in. if it contains more sulphur; ore larger than 3 in. is likely to form kernels (§ 54). These general figures will undergo slight changes with the character of an ore as dictated by practical experience.

<sup>1</sup> Wendt, *Sch. Min. Quart.*, 1885-86, VII, 173.

<sup>2</sup> *Op. cit.*, p. 180.

The ore is crushed by machinery (rock breakers) or by hand (spalling). The former works cheaply, but makes many fines; the latter permits sorting out barren rock and may thus compete with the former in small plants. However, crushed ore can be conveyed by picking belts and barren rock removed. The crushed ore is sized into three classes: coarse, 1 to 3 in.; medium (ragging) 1 in. to 3-mesh; fine, under 3-mesh. The sizing is done by grizzlies, trommels, or shaking screens; if hand labor is employed, by forking out the coarse, and separating the undersize by shoveling on to an inclined screen. The relative amounts of the sizes obtained in crushing vary greatly; thus, Peters<sup>1</sup> gives coarse 55, ragging 25, fines 25 per cent., and Glenn<sup>2</sup> coarse 82, ragging 7, fines 11 per cent. as average figures for the product.

(5) THE HEAP (Figs. 49-51).—The most important dimension of a heap is its height which varies with the percentage of S. An ore with 15 per cent. S can stand a height of 8 ft. above the bed of wood; one with over 35 per cent. S only about 5 ft.; an average height is about 6 ft. The length and width have little influence upon the result of the roast; large heaps which burn a long time are, however, more advantageous than small ones, as both furnish about the same amount of imperfectly roasted ore, which has to be retreated. Examples are given in Table 19.

(6) BUILDING OF HEAP.—The rectangle, 24×40 ft. in Fig. 50, is staked out, and fines, *a*, are spread over the ground to the depth of 4, 6, and even 8 in. They prevent roasting ore from adhering to the ground, are in part roasted and caked, so that they can be reroasted in a neighboring heap with lump ore. On to the fines is placed a bed of partly seasoned cordwood 3-5 in. thick and 4 ft. long. The best quality goes to form the border, which is 4 ft. wide and 8-14 in. (av. 9 in.) high; inferior uneven wood serves to fill the center. Work is begun by making the border *b*, which ends 6 in. from the staked lines. Sticks are laid down on the ends and sides of the proposed heap, placed end to end and parallel with the ends and sides of the heap, the side-borders butting against the end-borders. Flues (not shown), 6-8 in. wide, communicating with central chimneys, *c*, are left open in the sides every 8 or 10 ft., to be filled with kindling; the chimneys, about 8 in. sq., are boards (nailed together) of sufficient length to reach above the finished heap. On to the first layer of cord wood and at right angles to it is placed a second layer, *d*, of best-seasoned wood so as to reach to the staked lines and thus extend 6 in. over the bottom layer. Not coming in contact with the floor, this second layer greatly facilitates firing. The wood is piled as closely as possible; any open spaces are filled with small dry sticks. Upon the sticks, *d*, forming the second layer, are placed crosswise three to four sticks, *e*, to form a support for the ragging and fines, and thus prevent them from rolling down while the heap is being built. The space, *f*, between the border is now filled with sticks of varying size. They are laid on the fines end to end and parallel with the sides, but overlapping one another (Fig. 51), so as to leave air-spaces open. The wooden chimneys, *c*, are now put in place on top of the

<sup>1</sup> *Op. cit.*, p. 90.

<sup>2</sup> *Op. cit.*, p. 353.

TABLE 19.—ROAST-HEAPS.

	Point Shirley, Mass.	Imagin- ary.	Capleton, Canada.	Stafford, Vt.	Ore Knob, N. C.	Kiswick, Cal.	Type Copper Co., B. C.	Mond Nickel Co., Ont.	Canadian Copper Co., Ont.
Size, ft., $l \times w \times h$ .....	.....	$40 \times 24 \times 6$	.....	$24 \times 50 \times 5$	$17 \times 20 \times 8$	$20 \times 500 \times 8$	$24 \times 50 \times 7$	$40 \times 80 \times 15$	$55 \times 100 \times 10-12$
Weight of ore, tons.....	100-250	240	100	350	150	15,000	300	2500-3000	1700-1900
Composition of ore:									
Gangue, per cent.....	.....	.....	.....	22	.....	4	57.c <sup>1</sup>	.....	30
S, per cent.....	.....	39	39	33	30	46	16.6	27-28	24
Fe, per cent.....	.....	.....	33	37	.....	38	12.0	.....	40
Cu, per cent.....	5-6	6	4	6	4.2	8	4.6	.....	1.5
Zn, per cent.....	.....	.....	.....	.....	.....	4	6.6	.....	.....
Ni, per cent.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Sulphide mineral.....	.....	.....	FeS <sub>2</sub>	FeS <sub>8</sub>	.....	CuFeS <sub>2</sub>	CuFeS <sub>2</sub>	.....	Fe <sub>7</sub> S <sub>8</sub> , CuFeS <sub>2</sub> (FeNi)S
Duration of roast, weeks.....	8	10	6	11	6	26	3-4	8	14-16
S in roasted ore, per cent.....	.....	7-8	.....	4.6	7.6	12	7 <sup>2</sup>	10-12	10-12
Days labor, per ton of ore.....	0.15	.....	0.3	0.132	0.14	0.03	.....	.....	0.9
Wood, cord, per ton of ore.....	0.05	.....	0.05	0.024	0.03	0.008	0.035	.....	0.05
Reference.....	3	4	5	6	7	8	9	10	11

<sup>1</sup> Incl. 37.3 barite; <sup>2</sup> sulphide-S; <sup>3</sup> Eggleston, *School Min. Quart.*, 1885-86, VII, 360; <sup>4</sup> Peters, "Copper Smelting," 1895, p. 108; <sup>5</sup> Howe, "Copper Smelting," 1885, p. 17; <sup>6</sup> Glenn, *Eng. Min. J.*, 1883, xxxvi, 32 and Howe, *loc. cit.*; <sup>7</sup> Eggleston, *Tr. A. I. M. E.*, 1881-82, x, 33; <sup>8</sup> Neilson, *Eng. Min. J.*, 1899, lxxviii, 457; <sup>9</sup> W. J. Watson, letter, March 13, 1911; <sup>10</sup> Private notes; <sup>11</sup> Private notes.



kindling-flues, the boards facing two opposite flues being made about 8 in. shorter than the others in order to insure the necessary communication. Fig. 49 shows that the central and main part of the heap, *g*, is made up of coarse ore. This receives a cover of ragging, *h*, and the latter a thin layer of fines, *i*. The coarse ore is dumped from the overhead cars on to the finished bed of wood or at first perhaps on a wooden platform to break the shock; some of the ore is piled around the chimneys to steady them, and the rest evenly distributed over the bed.

In order to do away with part of the hand labor necessary for spreading the ore delivered at the center, a movable table, similar to the one shown in Fig. 52, is placed on the main track and connection made by two heavy rails held together by clamps and supported at one end by a bent. This permits dumping the ore on different parts of the heap. The first 3 ft. of coarse ore is piled carefully, and the sides are kept smooth and at as steep an angle as possible (42 deg.); the lower edge of the truncated pyramid of coarse ore reaches to within 2 to 2.5 ft. of the upper layer of cord wood. Top and sides of coarse ore are now covered with about 1 ft. of ragging, which grows a little thicker toward the bottom. The fines, about 10 per cent. of the weight of the ore, are arranged in small piles, about 3 ft. from the heap, so as to be ready for spreading later on the heap; or, one-third of the total is spread evenly over the heap, leaving uncovered the top and a border about 20 in. wide along the bottom.

(7) FIRING.—The firing of a heap is started early in the morning on a bright day. If there are no draft-flues, the firing is begun at the ends, otherwise the kindling in the flues is ignited. The bed of wood will be burning fully in from 4 to 6 hr. after starting, and the ore starting to roast. When the burning of the ore has progressed about 1 ft., a thin layer of fines is spread over the surface with a shovel and patted down. This smothering is continued as the fire creeps up, leaving visible a border of ignited ore. When the heap is well started, dense yellow fumes arise, the surface becomes damp (sweats), the heap settles, and fissures appear which are filled with fines. About the third day, the fire will have reached the top, when a workman ascends the heap and covers it with a layer of fines. The sides of the heap will show sublimed S, and  $As_2S_3$ , if the pyrite was arsenical; if the S is melted the temperature is too high; if the ore is cemented together by the S, the crusts formed have to be broken. The temperature on the sides and top must be kept even; it is correct when the hand can just bear touching the cover. If too hot, the thickness of the fines is increased; if too cool, it is decreased in order to draw the fire in the direction of the cool place. An average thickness of fines is 4 in. on the top and 3 in. on the sides. After 10 days, a heap requires little more attention than a daily inspection.

In some European works treating pyritic ores rich in S, sublimed S is collected on top of the heap during the first period by making in the cover 25 or more spherical depressions, 14 in. in diameter and 7 in. deep, lining them with raw or roasted fines, and enclosing the top of the heap with boards to protect the S from the prevailing air-currents. Nevertheless much S is burnt off; that which

remains, about 1 per cent. of the S of the ore, is ladled into wooden molds, refined, and sold.

(8) OPENING (STRIPPING, TURNING) OF HEAP.—This begins when roasting has ceased, and the heap has cooled sufficiently to allow transferring the ore to the feed floor of the blast-furnace. First, the heap is stripped, that is, unroasted fines and ragging are removed and transferred to a neighboring heap that is building; the rest then is pulled down, well roasted ore being kept separate from that which is imperfectly roasted or fused (heap-matte), the last two going to another heap that is being built. Heap-matte often has to be blasted.

(9) THE PRODUCTS are: (a) well-roasted ore which is porous, reddish-brown ( $\text{Fe}_2\text{O}_3$ ) to brownish-black ( $\text{Fe}_3\text{O}_4$ ), light, more or less friable; has an earthy fracture; and retains 4–7 per cent. S, the S-content rising and falling with the percentage of Cu, as most of the S is sulphide-S in combination with Cu; (b) imperfectly roasted ore, mostly fines and some ragging; (c) sintered and fused ore, a gangue-skeleton near the top, from which matted sulphide has eliquated and collected on the bottom. The proportions of these three products vary, but  $a:b:c=90:7.5:2.5$  are not uncommon.

(10) THE COST<sup>1</sup> is given as ranging from 20 to 80 cents per ton of ore. This great difference is caused mainly by the handling of raw and roasted ore as shown clearly in the costs of Keswick, Cal.,<sup>2</sup> given in Table 20, where labor was \$1.85 for 10 hr., wood \$3.00 per cord, and the daily capacity from 500 to 800 tons.

TABLE 20.—COST OF HEAP-ROAST  
Cents per Ton

Building heap and roasting	Indirect <sup>3</sup> loading	Direct <sup>1</sup> loading	Discharging heap	Manual labor	Steam shovel $\frac{3}{4}$ -yard capacity
Labor.....	15.00	6.25	Labor.....	20.50	4.50
Cordwood.....	2.50	2.50	Repairs.....		0.10
Poles abandoned.....	0.20				
Lumber and rails.....	0.16	0.54	Interest.....		0.20
Stores.....	0.04	0.02	Stores.....	2.50	0.12
Total.....	17.90	9.31		23.00	4.92
Grand total.....				40.90	14.23

The differences in arrangement for building, 17.90 vs. 9.31 cents per ton, and for discharging by hand or machinery, 23.00 vs. 4.92 cents, are made evident.

With the Tyee Copper Co. at Ladysmith, B. C., with labor at \$1.00 and fore-

<sup>1</sup> Church, *Eng. Min. J.*, 1893, LVI, 666.

Peters, "Modern Copper Smelting," 1895, p. 132.

<sup>2</sup> Neilson, *Eng. Min. J.*, 1899, LXVIII, 458.

<sup>3</sup> Indirect loading is the method described on page 75. Direct loading means that the ore screened at the mine was brought in 100-ton cars on a strong trestle running over the yard and discharged direct without any intermediate process, thus saving bunkers, grizzlies, tram cars, and small trestle. When one series of heaps had been built, the bents were transferred to another.

man at \$3.00, the cost per ton was: Laying wood, 0.007 cents; tramping from receiving lines to heap, 3.590 cents; shoveling from heaps to 2-ton cars ( $\frac{1}{3}$  of heap to be broken up with wedges), 15.490 cents; cordwood at \$2.00, 0.700 cents; total 19.787 cents; tramping by horse 1500-2000 ft. from yard to blast-furnace, 5 cents per ton.

Examples in addition to those given in Table 19 are: V-method of Peters and MacArthur<sup>1</sup> at Sudbury, Ont., given up as being of little advantage; roasting bituminous shale at Mansfeld, Germany;<sup>2</sup> roasting at Rio Tinto;<sup>3</sup> kernel roasting at Agordo;<sup>4</sup> and at Ducktown, Tenn.<sup>5</sup>

The two main advantages<sup>6</sup> of the process are cheapness of plant and process, with lump ore as a product. The main disadvantages, slow, imperfect, intermittent roast depending upon the state of weather; loss of ore by dusting, tramping under foot and leaching; locking up of large amounts of ore in an extended roast-yard; loss of S; killing of vegetation; and exclusion of fines in excess of say 10 per cent. The last is remedied in part by briquetting (Tyee Copper Co.) or moistening with  $\text{FeSO}_4 + \text{aq.}$  and allowing to harden (Agordo).

**57. Roasting in Stalls.**<sup>7</sup>—A stall is an oblong space surrounded on three sides by permanent walls; the fourth side, the front, when the stall is to be filled, is closed, wholly or only in part, by brick set dry or by an iron plate; the front wall is removed again when the stall is to be emptied. Frequently a number of stalls are built side by side against a main wall forming a single row as, *e.g.*, at Keswick, Cal.<sup>8</sup> Another arrangement is to have two rows of stalls, back to back with a main flue between them, Figs. 52-53. It is more compact, requires less brick and ironing (if not built of slag brick), retains the heat better, and makes it convenient to carry off the gases. The top of a stall is either open as in Fig. 53, or closed by a brick arch<sup>9</sup> or an iron plate. Ore-stalls are usually open, while matte-stalls are closed. Closing the stall gives a better utilization of heat, and insures withdrawal of gases through flues in the back or pipe in the roof.

Figs. 52-53 represent the stalls of the Butte Reduction Works, Butte, Mont., with some modifications. They are very similar to those formerly used at the

<sup>1</sup> *Tr. A. I. M. E.*, 1889-90, XVIII, 284.

<sup>2</sup> Jungfer, *Berg. Hüttenm. Z.*, 1887, XLVI, 471.

Egleston, *School Min. Quart.*, 1890-91, XII, 85.

Wagner-Primrose, *Eng. Min. J.*, 1907, LXXXIV, 673.

<sup>3</sup> Peters, *Min. Ind.*, 1893, II, 26.

Chalon, *Rev. Un. Min.*, 1902, LVII, 201.

<sup>4</sup> Church, *Eng. Min. J.*, 1872, XIV, 131.

Egleston, *School Min. Quart.*, 1887-88, IX, 124, 256, with cross references.

Ernst-Monaco, *Berg. Hüttenm. Z.*, 1891, I, 26.

<sup>5</sup> Wendt, *School Min. Quart.*, 1885-86, VII, 218.

<sup>6</sup> Henrich, *Tr. A. I. M. E.*, 1895, XXV, 224.

<sup>7</sup> Peters, *Min. Res.*, U. S. Geol. Surv., 1882, p. 290; 1883-84, p. 389; "Modern Copper Smelting," 1895, p. 40.

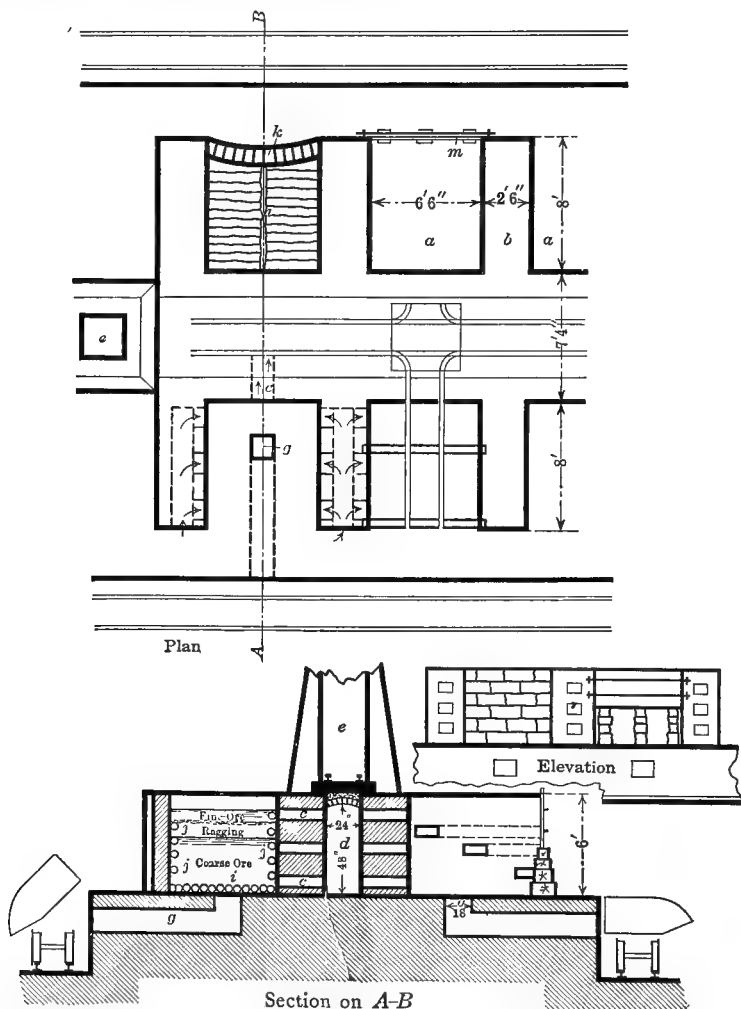
Henrich, *Tr. A. I. M. E.*, 1895, XXV, 229, 232.

<sup>8</sup> Keller, *Min. Sc. Press*, 1896, LXXIII, 497.

<sup>9</sup> Wendt, *School Min. Quart.*, 1885-86, VII, 306.

Parrot Smelter, Butte.<sup>1</sup> A stall, *a*, is 8 ft. deep, 6 ft. 6 in. wide, 6 ft. high, and holds about 20 tons average Butte ore.

The larger the stall, the more difficult the regulation of the air-supply and thereby of the temperature; hence small stalls are the rule. Large stalls have



FIGS. 52-53.—Roast-stalls of Butte Oil Reduction Works (with additions).

been failures as, *e.g.*, the older stall of the Parrot Works,<sup>2</sup> 40 ft. long by 9 ft. high, and the later one at Keswick, Cal.,<sup>3</sup> 14 ft. long by 7 ft. wide by 6 ft. deep, holding 35 tons.

<sup>1</sup> Peters, *Min. Res.*, U. S. Geol. Surv., 1883-84, p. 389; "Modern Copper Smelting," 1895, pp. 148-150.

<sup>2</sup> Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 261.

<sup>3</sup> Keller, *Min. Sc. Press*, 1896, LXXIII, 497.

Neilson, *Eng. Min. J.*, 1899, LXVIII, 457.

The walls, *b*, are usually of slag brick, as these are cheap and little attacked by the roasting ore; they are made very thick, 2 ft. 6 in. to 2 ft. 9 in., in order to require no ironing. The back wall has three openings: *c*, 6 by 8 in., for the passage of the gases into the main flue *d*, 24 by 48 in., leading into the stack *e*, 3.5 ft. square by 75 ft. high. The flue is provided with a damper (not shown). With this arrangement, characteristic of the older stalls, air enters only at the front. In order to allow admission of air at the sides and the bottom, modern stalls have flues, *f*, in the side-walls, and usually a single one, *g*, in the floor which has a grated intake. The air-supply can be reduced or shut off by placing bricks in the flues. As a carefully regulated admission of air is essential for good work, the roasting in modern stalls is more satisfactory than in the older type.

Before a stall is charged, the walls are usually plastered with clay to prevent adhesion of roasting ore. The manner of placing the fuel-bed varies. A central air-passage from front to back with two cross-ways is built with lump ore, filled with kindling, and the whole covered with rotten wood (sound cordwood often gives too much heat), or the cross-ways are omitted as with *h* in Fig. 52. Upon the bed of wood is charged coarse ore, *i*, then coarse and ragging, placing here and there sticks against side and back walls to prevent chilling, and light wood toward the front, as this is being built of coarse ore backed by brick laid dry and in the form of an inverted arch, *k*; then comes ragging alone followed by a 3- or 4-in. layer of chips of wood, bark, shavings, etc., which is covered with from 1 to 1.5 tons of fines. At the Butte Reduction Works the front of the stall is closed down to 2 ft. from the bottom with a plate of sheet iron, *m*, braced by cross-bars to prevent bulging and supported by wooden blocks, *n*, small sticks and kindling being placed between the latter. When the swelling of the ore during the roast has caused the charge in the stall to rise to its maximum and it begins again to shrink, the front plate gradually glides down to the floor.

A stall is usually fired at night, as the draft is better than during the day and carries away most of the offensive smoke that arises at first in considerable amounts. After the first day, the lower part of the front brick wall is warm; after the second the middle part, and after the fourth day the upper part. The roast is finished after nine days, when the front wall is taken down, the stall entered and its contents removed. Butte sulphide copper ore loses about 15 per cent. in weight and rises as much as 12 in. during the roast; if instead the surface sinks, there is furnished proof that the heat was too great or the admission of air insufficient, both of which would cause fusion.

The stall in Figs. 52-53 holds 20 tons ore, requires 8-9 days for roasting, or 10 days between charges. Thus a stall treats 2 tons per day and, assuming 15 per cent. loss in weight by roasting, there will have to be roasted about 120 tons of raw ore to furnish 100 tons of roasted ore, and this demands 60 stalls. The cost of roasting lump ore in seven stalls, each with a capacity of 25 tons, as estimated by Henrich,<sup>1</sup> is 1 roast-yard foreman \$2.25; 3 men preparing seven empty stalls and laying wood-foundation, at 50 cents per stall, \$3.50; 8 men

<sup>1</sup> *Tr. A. I. M. E.*, 1895, XXV, 232.

filling seven stalls, building front walls, ready for firing, at \$1.50 per stall, \$10.50; 14 men emptying seven stalls, at \$2.50 per stall, \$17.50; 4 cords of wood at \$1.55, \$6.20; 200 hard-burnt brick, at \$5.00 per M., \$1.00; tools, oil, repairs, clay, etc., \$7.55; unforeseen expenses, \$5.00; total for 175 tons, \$53.50, or 30.57 cents per ton.

The advantages of stall-over heap-roasting are: A more uniform distribution and better utilization of heat, hence a smaller amount of wood; a smaller loss of ore by scattering and leaching; a quicker roast, requiring a smaller locking-up of ore; easy disposal of gases. The main disadvantages are: Cost of plant; greater cost of labor; close attention to process on account of danger of insufficient roast or of fused charge. At Keswick, Cal.,<sup>1</sup> stalls were replaced by heaps. In general, stalls will be used only with small amounts of coarse sulphide ore.

**58. Roasting in Shaft Furnaces (Kilns) in General.**<sup>2</sup>—The furnaces are shaft-like structures of varying heights in which the ore rich in S is roasted without the use of carbonaceous fuel, the oxidation of S and Fe furnishing the necessary heat. The process is continuous, raw ore being charged periodically at the top and roasted ore drawn at the bottom; the gases containing over 4 per cent. vol. SO<sub>2</sub> and being free from carbonaceous matter are suited for the manufacture of SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, or H<sub>2</sub>SO<sub>3</sub>. The furnaces are usually classed as lump-ore and fine-ore furnaces. Lump ore ranges in size from  $\frac{1}{4}$  (perhaps  $\frac{1}{2}$ ) to 3 in., a piece larger than 3 (perhaps 3.5) in. not being satisfactorily desulphurized in the center; the actual size within the range is governed by the more or less free-burning character of the ore. It may be necessary to carry the sizing farther and separate the coarse into three classes, 0.25–1.00, 1.00–2.00, 2.00–3.00 in. in order to obtain the best results. Fine ore, smaller than 0.25 in., is roasted separately. A lump ore cannot stand more than 10 per cent. fines; a larger amount blocks up the air-passages, which results in imperfect roasting and in clinkering.

**59. Roasting Lump Ore in Shaft Furnaces.**—The ore, in which pyrite is the usual sulphide, may not contain less than 25 per cent. S, if the S-content is to be reduced to below 4 per cent.; the lower limit in the eastern United States is 37 per cent. Usually the pyrite ore charged contains over 40 per cent. S. The ore, further, should not be rich in Pb (10 per cent. causes clinkering), in Cu (< 8 usually < 5 per cent.), as chalcopyrite, the common form of copper mineral, decrepitates upon heating, causes clinkering, and furnishes gas low in SO<sub>2</sub>. The best material is coarse (< 8 per cent. fines), hard, non-decrepitating pyrite with < 6 per cent. gangue, and < 5 per cent. Cu. Thus<sup>3</sup> Spanish, Portuguese, some

<sup>1</sup> Neilson, *Eng. Min. J.*, 1899, LXVIII, 458.

<sup>2</sup> Jurisch, K. W., "Handbuch der Schefelsaeurefabrikation," Enke, Stuttgart, 1893.

Lunge, G., "Sulphuric Acid and Alkali," Gurney and Jackson, London; Van Nostrand, New York, 1913, I, pp. 415–501.

Wilson, W. G., "Pyrites in Canada," *Canada Dep't. Mines*, Mines Branch, Ottawa, 1912, pp. 94–132, "Roasting of Pyrites."

Wyatt, *Eng. Min. J.*, 1887, XLIV, 165.

Falding, *Min. Ind.*, 1898, VII, 665.

<sup>3</sup> Falding, *loc. cit.*

Norwegian and Newfoundland ores contain 48 per cent. available<sup>1</sup> S and 3-4 per cent. Cu; pyrite from New England,<sup>2</sup> northeastern Canada, New York, and Virginia, 35 per cent. available S and < 3.5 per cent. Cu. Pyrrhotite in lump form does not roast satisfactorily in kilns.

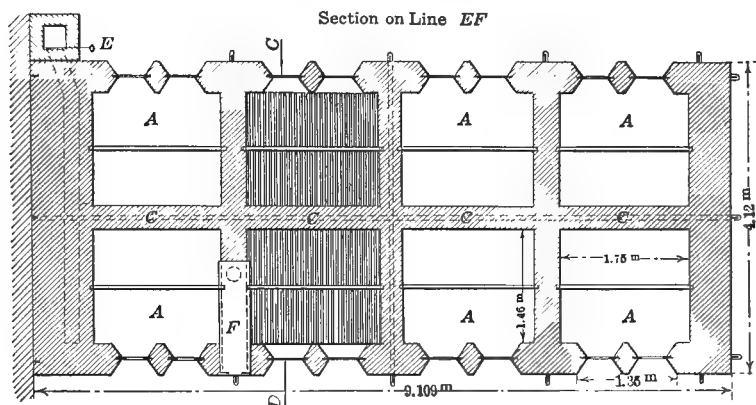


FIG. 54.—Oker pyrite-kiln.

**FURNACE.**—The furnace for burning pyrite is essentially a rectangular brick chamber 5-6 ft. sq. and 4-6 ft. high, with doors at the front for charging, stirring, and discharging, and an opening in the roof for carrying off the gases. In the chamber there are horizontal grate-bars reaching from front to back which carry the ore. The depth of the charge is regulated by the size and S-content of the ore, as is the draft, and with this the rate of roasting.

(1) **THE OKER KILN.**<sup>3</sup>—A block of eight kilns built in two rows of four, back to back, is shown in Figs. 54-55. *A* is the roasting chamber 5 ft. 9 in. wide, 4 ft. 9 in. deep, and 3 ft. 3 in. high; *B* grate; *C* center wall; *D* flue for roaster gas, covered with cast-iron plates, on which rests a lead pan for concentrating dilute  $H_2SO_4$ ; *E* damper; *F* chamber for iron or lead vessel charged with  $NaNO_3$  and  $H_2SO_4$  to generate  $N_xO_y$ -fumes, which pass through vertical circular, uptake *D*; *G* cinder pit with car to receive roasted ore through grate by rocking; the ends of the pit are closed by folding or sliding doors. The movable grates

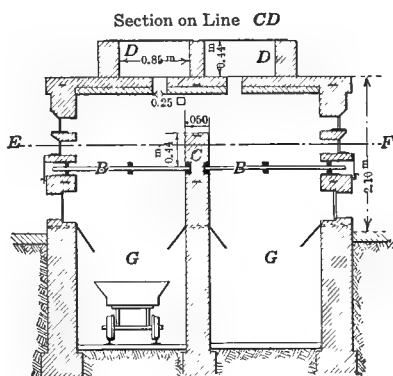


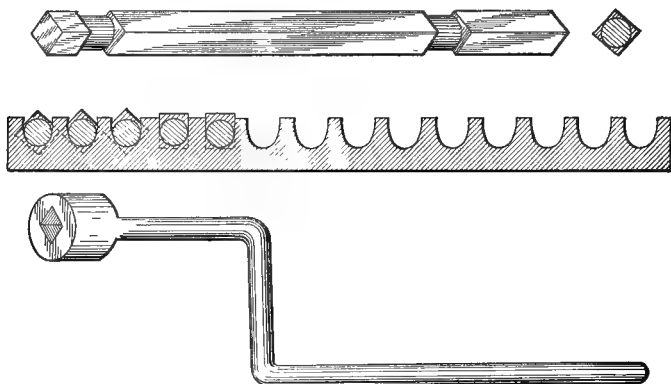
FIG. 55.—Oker pyrite-kiln.

<sup>1</sup> This is the S remaining after the amount held back by constituents such as Zn, Cu, Pb, Ca, Mg in the form of sulphide or sulphate has been deducted from the total.

<sup>2</sup> *Min. Res.*, U. S. Geol. Surv., 1885, p. 501.

<sup>3</sup> Bräuning, *Zt. Berg. Hütten. Salin. Wesen.*, i Pr., 1877, xxv, plate iv. For other drawings see Treatises of Lunge and Jurisch, and paper by Falding, *Min. Ind.*, 1908, vii, 666.

(Figs. 56-57) are square wrought-iron bars made circular in the bearing places so that they can be rocked by means of a T-handle key. By setting the bars on edge, the open spaces between them are smallest; when flat on the sides the spaces are largest; when alternately on edge and on side, the size of the open spaces is between the above extremes. Ore is fed from the front through the upper door, which otherwise is closed by a cast-iron plate, the joint being made air-tight by a clay lute. The central door, through which access is had to the grate bars, is closed by a hinged cast-iron door. The lower opening has a sliding door for regulating the admission of air. The ore-bed is only 1 ft. 5  $\frac{3}{8}$  in. high. The eight kilns roast in 24 hr. 3.5 tons of pyrite 1.25 in. in diameter with 40 per cent. S, or 35 lb. of ore per square foot of grate area, the S being reduced to 4 per cent.; with ore assaying 6-9 per cent. Cu, the roasted ore retains 5-6 per cent. S.



FIGS. 56-57.—Shaking-grate of lump-ore roasting-kiln.

The leading operations are drying and heating, charging and discharging, loosening up, and regulating the air-supply. With the damper in the gas-flue closed, the furnace is dried by having a low fire on the grate and allowing the smoke to pass into the building through the charging doors. When dry, the roasting chamber is filled with burnt ore or with pebbles to about 3 in. below the charging door, and a wood or coal fire started upon the bed and kept going for about 24 hr.; this will bring the upper layer of the bed as well as the roof to a dark red, whereupon, pyrite is charged, which will kindle and burn. When burning freely, the charging door is closed and the damper in the gas-flue opened. A kiln is usually fed every 12 hr.; fines are spread mainly along the sides, and some are scattered over the surface of the coarse ore. A charge weighs from 700 to 1000 lb.

Roasted ore is discharged before feeding raw ore. Sometimes it precedes the feeding as much as 2 hr. in order that the ore-bed, loosened and freed from dust by the rocking of the grates, may roast freely and be thus better prepared for receiving the cold charge. The grate may need shaking between chargings in order to remove fines in the crumbled roasted ore. Any packing or caking of roasting ore is corrected by inserting a slice bar or poker. A furnace is in good



working order when the charging door is too hot to permit touching with the hand, and when the air-inlet door is just warm. The success of roasting depends upon the air-supply (an excess gives dilute gas, a lack causes clinkering), the depth of bed (an excess gives too high a temperature, a lack insufficient desulphurization), the percentage of fines (an excess chokes the draft and causes clinkering), and the rate of discharge (an excess gives imperfectly roasted ore, a lack reduction of capacity). The temperature of the escaping gas should not exceed  $420^{\circ}$  C. Table 21<sup>1</sup> gives the distribution of Cu-Fe-S-compounds in 5 samples of kiln-burnt pyrite.

TABLE 21.—DISTRIBUTION OF CU-Fe-S COMPOUNDS IN KILN-BURNT PYRITE,  
Per cent.

CuSO <sub>4</sub>	CuO	Cu <sub>2</sub> S	CuFeS <sub>2</sub>	FeS <sub>2</sub>	Fe <sub>2</sub> .(SO <sub>4</sub> ) <sub>3</sub>
5.55	0.89	1.55	0.69	2.35	0.59
1.67	0.76	3.76	1.09	1.56	0.55
3.45	1.26	2.54	0.00	4.32	2.25
0.55	0.46	1.27	0.72	7.34	2.29
0.82	0.25	0.51	0.35	5.90	0.68

Dimensions and work of some coarse-ore kilns are given in Table 22.<sup>2</sup>

TABLE 22.—DIMENSIONS AND WORK OF COARSE-ORE ROASTING KILNS

Ore, source and kind	Sulphur, per cent.	Grate area, sq. ft.	Ore-bed, depth, in.	Ore roasted, lb.	
				in 24 hr.	per sq. ft. grate area
Harz Mts.....	44	28.21	18.5	965	34.2
Low grade.....	41	24.97	26.4	895	35.8
General.....	39	24.76	26.4	1008	40.6
Ireland.....	42	22.72	36.2	895	39.7
Portugal.....	49	22.72	31.5	895	39.7
Spain.....	48	10.75	21.7	397	37.3
Spain.....	48	25.00	26.4	787	31.5
Spain.....	49	21.64	24.0	992	45.9

A block of over twenty furnaces is in charge of two men; with a 1000-lb. charge of ore per kiln in 24 hr., this gives 0.4 day labor per ton of ore. Usually, however, the blocks are smaller, as is the weight of charge; the labor necessary is correspondingly increased.

(2) THE FREIBERG KILN, SAXONY.—This kiln, shown in Figs. 58–59,<sup>3</sup> is an oblong shaft furnace, 8 ft. high by 4 ft. 6 in. wide by 7 ft. 6 in. long; it has on the floor a saddle, *g*, of cast-iron plates, which deflects the roasted ore toward the discharge-openings *f*, through which the air necessary for roasting enters. Raw ore is delivered to the receiving hopper *a*, and discharged through chutes *b*,

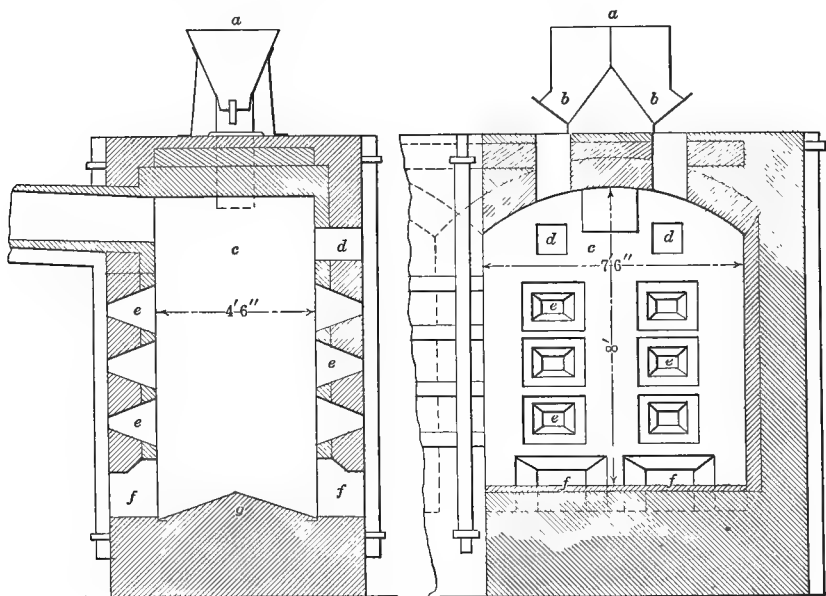
<sup>1</sup> Kothny, *Oest. Jahrb.*, 1910, LVIII, 107; *Metallurgie*, 1911, VIII, 390.

<sup>2</sup> Jurisch, *op. cit.*, p. 73.

<sup>3</sup> Lunge, *op. cit.*, p. 421.

into the furnace *c*; doors *d*, serve for spreading charge, and *e* as working doors. Five furnaces form a block. The material roasted is either pyritic ore with  $< 40$  per cent. S, containing blende and arsenopyrite, or lead and copper matte with  $22 \pm$  per cent. S. About 2,500 lb. pyritic ore is roasted in a kiln in 24 hr. The S-content is reduced to 4–5 per cent.

The original furnaces of Oker have been reconstructed on the lines of the Freiberg kilns. There are two types: one for medium-S ore having a bed 6 ft. high, the other for low-S ore with a bed 9 ft. high. Ore consisting of ZnS 28, FeS<sub>2</sub> 25, CuFeS<sub>2</sub> 15, PbS 11 per cent. has its S-content reduced to 10–12 per cent.



FIGS. 58–59.—Freiberg coarse-ore kiln.

Matte with 30–50 per cent. Cu clinkers in the kiln if roasted alone; it is satisfactorily rough-roasted when mixed with 25 per cent. in weight of similar matte that has passed once through the kiln.

The furnaces at Kedabeg, Caucasus,<sup>1</sup> are 7 ft.  $2 \frac{5}{8}$  in. by 3 ft.  $11 \frac{1}{4}$  in. and 11 ft.  $1 \frac{7}{8}$  in. high. A double furnace treats in 24 hr.  $9 \frac{1}{2}$  tons of pyritic ore with  $> 5$  per cent. Cu and  $> 0.5$  in. in size, reducing the S-content to 8–10 per cent.

**60. Comparison of Heaps, Stalls, and Kilns.**—A comparison of the three roasting apparatus shows that kilns have the advantage in that the process is continuous, independent of the weather, requires less time, gives a better elimination of S, and needs no fuel; the S can be recovered; there is practically no mechanical loss, nor any leaching-loss whatever. The disadvantages are the great size and cost of plant per unit of daily product, and the necessity of skilled

<sup>1</sup> Koelle, *Tr. Inst. Min. Met.*, 1904–05, XIV, 508.

Golowatschew, *Glück Auf*, 1913, XLIX, 733, transl. by Hahn, *Eng. Min. J.*, 1913, XCVI, 15.

labor. In general, kilns are used only where there is profit in or necessity of not allowing the sulphurous gas to escape into the air.

**61. Roasting Fine Ore in Shaft Furnaces.**—Fine ore is produced in mining (mine-fines), in breaking coarse ore for kilns (smalls), and in ore-dressing plants (concentrates).

In sulphuric-acid works the mineral commonly roasted is pyrite; in metallurgical plants other metallic sulphides often take its place. Attempts to make sulphuric acid from the gases obtained in roasting pyrrhotite were so unsatisfactory that the mineral was condemned as a raw material until Sjöstedt<sup>1</sup> showed in the sulphurous acid plant at Sault Ste. Marie, Ont., that with pyrrhotite assaying 24.46 per cent. S a gas averaging 7.91 per cent. vol. SO<sub>2</sub> was obtained. The S in the roasted ore was brought down to 1.81 per cent., provided the loss of heat by radiation was reduced to a minimum by combining 4 furnaces of the MacDougall type in a single block, and by enclosing this with a bad conductor of heat.

The furnaces used for roasting fine ore are oblong or circular shaft-like structures into which the ore, fed intermittently or continuously at the throat, meets during its descent horizontal or inclined shelves, or prisms, which retard its downward progress sufficiently to effect the desired degree of desulphurization. The furnaces, provided with chambers to settle out dust, do satisfactory work with ores that run high enough in S (about 28 per cent.) to sustain combustion and do not become sticky while roasting.

At first, fines were pugged with clay, 10 per cent. or more, and made into balls which, when air-dry, were roasted to the extent of perhaps 16 per cent. with coarse ore. Very fine dust pugged with water alone, molded and exposed to warm air, vitriolized superficially, hardened, and thus furnished a material that could be treated together with coarse ore. Untreated fines have been roasted in connection with coarse-ore furnaces, the gases from the latter serving to burn the fines (Olivier Perret, older Haasenclever-Helbig furnaces<sup>2</sup>). These devices and furnaces which were formerly the transition between coarse- and fine-ore furnaces have become obsolete.

The fine-ore furnaces proper may be classed (1) as Automatic, in which the ore glides downward through a shaft; and (2) as Shelf-burners, in which the ore is moved from shelf to shelf either by hand or mechanically.

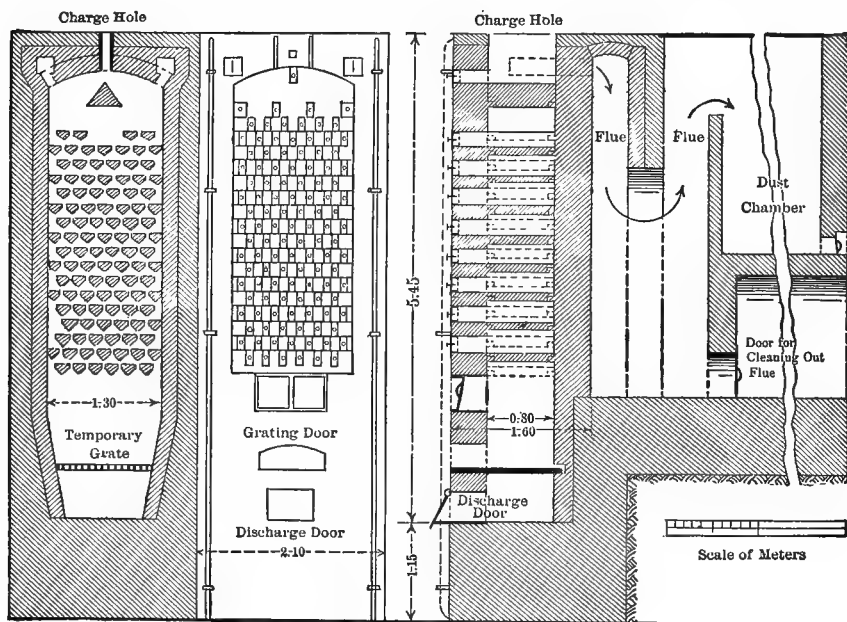
**62. Automatic Furnaces. THE GERSTENHÖFER FURNACE.**—This is shown in Figs. 60–61. It is the only automatic furnace which is still in operation in a few plants. It consists of a shaft 17 ft. high, 2 ft. 7½ in. wide, and 2 ft. 3 in. deep, which contains from 15 to 17 horizontal tiers of staggered triangular fire-brick bars, 6 or 7 bars to a tier. The ore, fed continuously by fluted rolls (not shown), drops onto the upper bars, accumulates until it reaches its angle of repose of about 33 degrees, then glides on to the bars below, and so on until it arrives at the bottom. The fresh ore flows downward and displaces the particles previously lying on the bars and takes their places. The air necessary for oxidation enters near the bottom and meets the descending ore; the furnace-

<sup>1</sup> *J. Canad. Min. Inst.*, 1904, VII, 480.

<sup>2</sup> *Lunge, op. cit.*, First Edition, 1879, pp. 193 and 200.

gases pass off on either side of the feed through flues leading into dust chambers. At the front of the furnace are openings, usually closed by cast-iron doors, to allow watching the process and inserting of tools to remove clinkers and clean the passages. The roasted ore is removed from the bottom of the shaft either by shoveling or by a screw conveyor.

In starting, a temporary grate is put in place, and a fire maintained on it until the shaft has been brought to a bright red. Firing is continued for from 6 to 7 hr. until the fourth tier of bars from the bottom begins to receive ore, when the grate is removed, and the damper of each of the flues leading into the



FIGS. 60-61.—Gerstenhöfer kiln.

dust chambers drawn out. The admission of air has to be well regulated, for an excess drives the heat up, and makes the furnace too hot; a lack draws it down, and cools the furnace. The furnace works with ore of 1 mm. size containing from 25 to 36 per cent. S; it fails with less than 25 per cent. S. It treats in 24 hr. from 2 to 5 tons of concentrate, reducing the S-content to from 8 to 10 per cent. The roast is therefore imperfect; much flue dust is formed, and repairs are likely to be costly. The furnace was first used at Freiberg, Saxony, in about 1866, but has been abandoned there; it was in operation in Swansea,<sup>1</sup> and is still in operation in Kedabeg, Caucasus.<sup>2</sup> At these works it has twice the width of the standard furnace; treats in 24 hr. 12.5 tons of pyritic ore, < 0.25 in., with over 5 per cent. Cu, reducing the S-content to 6 per cent. The latest report<sup>3</sup> of this plant

<sup>1</sup> Vivian, *Eng. Min. J.*, 1881, XXXI, 231.

<sup>2</sup> Koelle, *Tr. Instit. Min. Met.*, 1904-05, XIV, 510.

<sup>3</sup> Golowatschef, *Glück Auf*, 1913, XLIX, 732; transl. by Hahn, *Eng. Min. J.*, 1913, XCVI, 15.

states that there are 10 furnaces. A furnace is 7 ft. 4 in. by 1 ft. 9 in. and 24 ft. 6 in. high; has four feed openings, 14 tiers of fire-brick bars (10 bars 6.9 in. wide to a tier) and two oil-fired fire-places at the front. A furnace treats in 24 hr. 11 tons of ore, consumes 572 lb. oil, reduces the S-content to 3 per cent., and makes 5 per cent. flue-dust in which the Cu is present mainly as  $\text{CuSO}_4$ .

**63. Shelf-burners.**—(1) THE MALETRA FURNACE.—Of the hand-raked shelf-burners that of Maletra constructed in 1867 was the first. A double furnace designed by Niedenführ is shown in Fig. 62.<sup>1</sup> The roasting-chamber, 9 ft. long by 3 ft. 11 in. wide by 6 ft.  $10\frac{3}{8}$  in. high, has seven horizontal shelves, made of  $3\frac{1}{2}$ -in. rebated fire-brick tiles, which extend over the entire width of the

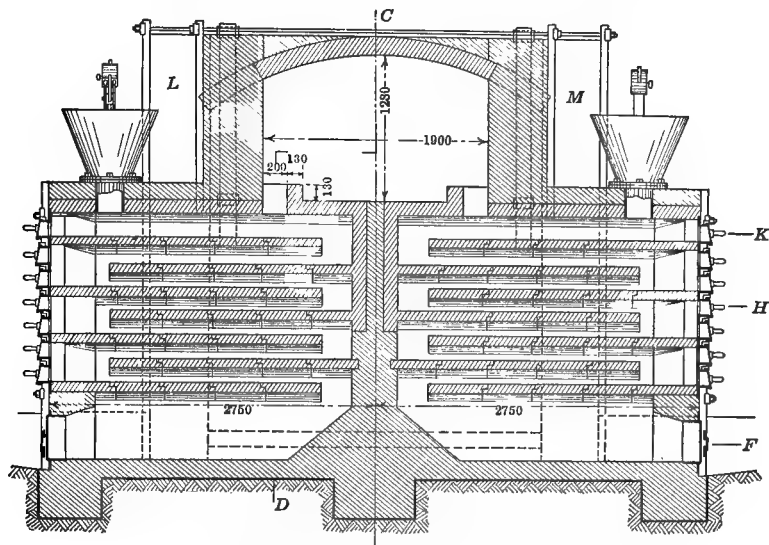


FIG. 62.—Maletra shelf-burner (dimensions in millimeters).

furnace, but are 9 in. shorter than the length of the furnace and are staggered so as to leave open spaces alternately at front and back. The distance between the upper two shelves is greater than that between the lower five; above the top shelf it is 7 in.; between shelves 1 and 2, 6 in.; the other shelves are 5 in. apart.

The ore, from dust to pea-size, is charged through a hopper in the roof, spread over the top shelf with a rabble or rake from the opening at the front, usually closed by a sliding door, and pushed after from 4 to 8 hr. through the slot on to the next lower shelf, when a fresh charge is dropped from the feed-hopper and so on. Air, admitted over the roasted ore in the pit, travels in a direction opposite to that of the ore; the gases deposit the suspended dust in part on the bottom of the flue connecting a set of kilns, in part in special dust chambers. The ore remains  $4 \times 7 = 28$  or  $8 \times 7 = 56$  hr. in the furnace. The roasted ore is moved from the chamber beneath the bottom shelf. In rabbling or in transferring ore as

<sup>1</sup>Lunge, *op. cit.*, I, <sup>1</sup>p. 468; other drawing by Falding, *Min. Ind.*, 1908, VII, 667.

little false air as possible ought to enter a furnace, as it dilutes the gas. Irregularities are avoided by having a number of furnaces in a block.

A new furnace is brought to a red heat by burning fuel on the shelves for 4 or 5 days. Furnaces are built in single or in double rows forming blocks with from 8 to 16 kilns. A furnace roasts in 24 hr. about 2200 lb. 50-per cent. pyrite, or 3200 lb. when of lower grade, or on the average from  $6\frac{1}{2}$  to  $7\frac{1}{2}$  lb. per square foot hearth area, reducing the S to 1 per cent. and lower. Pyrite ought to contain not less than 38 per cent. S.

Table 23 gives some data for a six-shelf furnace<sup>1</sup> charged every 4 hr., and for a seven-shelf furnace<sup>2</sup> charged every 8 hr.

TABLE 23.—RESULTS OF THE MALETRA FURNACE

Raw pyrite	S, per cent. 49.65	Tem- perature, ° C.	After hours	Raw pyrite	S, per cent. 50	After hours	Raw pyrite	S, per cent. 50	After hours
Shelf 1....	37.90	680	4	Shelf 1...	32.27	8	Shelf 1...	32.81	8
Shelf 2....	30.13	750	8	Shelf 2...	21.41	16	Shelf 2...	17.55	16
Shelf 3....	10.10	720	12	Shelf 3...	12.77	24	Shelf 3...	11.09	24
Shelf 4....	1.26	650	16	Shelf 4...	6.39	32	Shelf 4...	5.05	32
Shelf 5....	1.08	380	20	Shelf 5...	4.08	40	Shelf 5...	3.42	40
Shelf 6....	0.59	310	24	Shelf 6...	2.35	48	Shelf 6...	2.56	48
.....	.....	.....	.....	Shelf 7...	2.27	56	Shelf 7...	1.96	56

Under normal conditions no blue flame is visible when the ore is transferred from shelf 1 to shelf 2; shelf 2 is bright-red, shelf 3 a shade darker and so on; the last shelf is dark. Just as in the Gerstenhöfer furnace, a draft that is too strong causes the heat to creep up and cool the lower shelves, the reverse holds good with a draft that is too weak; in either case the ore on the hottest shelf begins to sinter. From four to five furnaces are given in charge of one man on each shift.

(2) THE SPENCE FURNACE.<sup>3</sup>—This furnace, shown in longitudinal vertical section in Fig. 63, is a shelf-burner in which the ore is mechanically fed from a hopper in the roof and then pushed at intervals from shelf to shelf by reciprocating rakes until it is discharged at the bottom into a car. The rakes of the several hearths are provided with trippers so that they will act upon the ore only in one direction; the rods are connected outside of the furnace to a frame which is moved to and fro at certain intervals by steam or hydraulic power (1–2 h.p.). The heads of the rakes when not in motion rest at the ends of the hearths on the parts of the shelves lying beyond the discharging slots. Thus a rake will travel over the hearth in  $1\frac{1}{2}$  min., come to a stop, rest for 5 min., and then make the return trip.

<sup>1</sup> Krutwig-Dernoncourt, *Rev. Univ. Min.*, 1898, XLI, 288.

<sup>2</sup> Crowder, *J. Soc. Chem. Ind.*, 1891, x, 298.

<sup>3</sup> Marten, *Min. Res.*, U. S. Geol. Surv., 1883–84, p. 892.

Adams, *Tr. A. I. M. E.*, 1884–85, XIII, 345.

Wendt, *School Min. Quart.*, 1885–86, VII, 322.

The hearth of a furnace is 5 ft. wide and varies in length; a hearth 5 ft. by 16 ft. 8 in. inside has a roasting area of only 5 by 10 = 50 sq. ft. The furnaces are usually built in pairs with a common middle-wall. A double furnace will treat in 24 hr. from 3 to 4 tons pyrite with 46 per cent. S, and reduce this to about 2 per cent., or about 70 lb. in 24 hr. per square foot of hearth area.

The original furnace has undergone several changes, notably at the hands of Adams and Hammond. The latter,<sup>1</sup> among other important alterations, has provided the furnace with a fire-place which may be used only for warming, or also continuously and thus change the kiln into a reverberatory furnace if the flame travels over the ore, or into a muffle furnace if it passes through flues

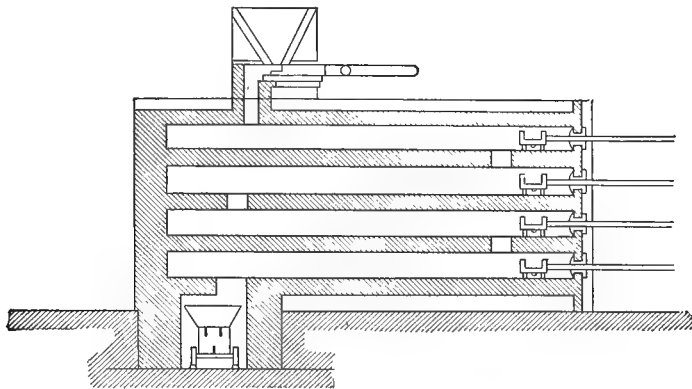


FIG. 63.—Spence automatic desulphurizing furnace.

placed between the hearths. In the United States the Spence furnace has been widely used in sulphuric acid plants, but has had to give way to the Mac Dougall type of kiln.

**64. The MacDougall Furnace in General.**<sup>2</sup>—This furnace is a vertical cylinder with superimposed horizontal hearths and central rotating shaft with radial stirring arms provided with teeth set at a proper angle. The ore, fed mechanically at the top, is turned over by the rabble arms, moved on one hearth from the periphery toward the center, where it drops through a slot on to the next following hearth to be moved in the opposite direction that it may drop through slots near the periphery on to the third hearth and continue to travel until it is finally discharged from the bottom into a receiver. During the fall of the ore from hearth to hearth a large part of the S and Fe in the ore is oxidized and the required heat generated.

The air necessary for oxidation enters through doors situated either wholly

<sup>1</sup> Peters, "Modern Copper Smelting," 1895, p. 221.

<sup>2</sup> Lunge, "Sulphuric Acid and Alkali," 1913, I<sup>1</sup>, 474.

Benker-Hartmann, *Zt. angew. Chem.*, 1906, XIX, 1125, 1188.

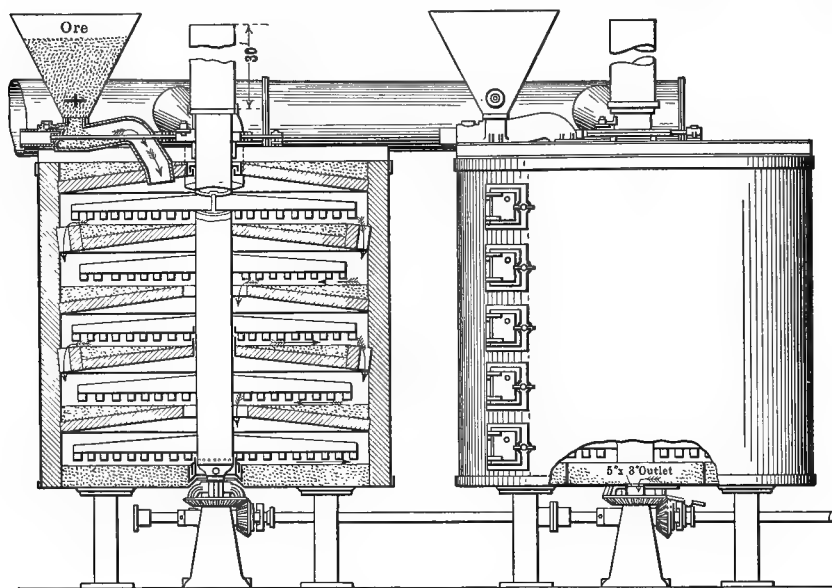
Pierron, *Rev. Chim. Ind.*, 1907, XVIII, 8.

Wilson, G. W., "Pyrites in Canada," Canada Dep't. of Mines, Mines Branch, Ottawa, 1912, pp. 101-125.

on the bottom hearth or in part on one or more of the upper hearths, and travels in a direction opposite to the ore. This type of furnace, being automatic, does uniform work at a low cost, and permits full control of air and temperature which means a good roast; on the other hand it makes a considerable amount of flue-dust.

The original furnace was in operation in Liverpool, England, about 1870, but was abandoned mainly on account of mechanical difficulties. In this country it was taken up again by Herreshoff in 1896, and later by others. The leading types at present are those of Herreshoff, O'Brien, Evans-Klepetko, with modifications, and Wedge.

**65. The Herreshoff Furnace.**<sup>1</sup>—The original form of this furnace, shown in Figs. 64–65, has four or five hearths, and a central air-cooled hollow shaft with



FIGS. 64–65.—Herreshoff furnace, original form.

pockets to receive the hollow rabble-arms. The shaft ends in a 30-ft. stack. An arm, Fig. 66, has on the upper side of the inner end a projection, *a*, which fits into a corresponding cavity, *b*, in the pocket *c*, and being thus hinged is held in place by its own weight.

The ore is fed mechanically near the center of the top hearth; the teeth forming part of the rabbling arms are placed at an angle in order that, traveling over the hearth, they may not only turn over the ore, but move it gradually toward the periphery, whence it drops through slots on to the second hearth. The

<sup>1</sup> The Nichols Copper Co., New York, N. Y. Herreshoff, *Min. Ind.*, 1897, VI, 235; 1902, XI, 205.

Gilchrist, *J. Soc. Chem. Ind.*, 1899, XVIII, 459.

Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 277.



teeth of the pair of rabble-arms of the second hearth point in the opposite direction enclosing an angle of the same magnitude as those of the first hearth; they therefore move the ore from the periphery to the slot near the center, and so on.

At the works of the Montana Ore Purchasing Co., Butte, Mont., there were in operation in 1899, 70 furnaces, 10 ft. 10 in. in diameter and 11 ft. 6 in. high, made of  $\frac{1}{4}$ -in. steel casing, lined with a full course of red brick. A few furnaces with two full courses of brick, hooped with iron bands, worked more satisfactorily in the cold winter than the rest. A furnace had five arched brick hearths  $4\frac{1}{2}$  in. thick and 11-12 in. apart, the pitch of the arch being  $4\frac{1}{2}$  in.; the central shaft was 14 in. in diameter, and each arm had seven or eight teeth. The top hearth

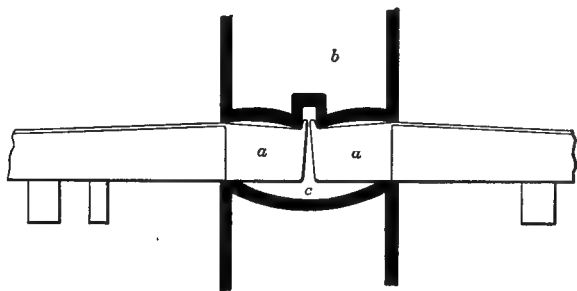


FIG. 66.—Rabble-arm of Herreshoff furnace, original form.

acted as a dryer for the wet concentrates fed, the second started the roast, on the third the ore was roasting freely with many sparks visible, on the fourth there was no sparking, on the fifth the ore appeared dark. With the shaft making 50 r.p.h., a furnace roasted in 24 hr. from 5 to 6 tons of wet concentrates with about 35 per cent. S, or 30 lb. per square foot of hearth area, reducing the S-content to 6 per cent. and making 6.4 per cent. flue-dust; the cost of roasting was \$0.40 per ton.

In eastern sulphuric acid plants the furnace treats in 24 hr., with the shaft making 30 r.p.h., from 3 to 4 tons of Virginia pyrite with 44 per cent. S. or Tharsis pyrite with 49 per cent. S, or 19.6 lb. per square foot hearth area, reducing the S to  $2\frac{1}{2}$ - $3\frac{1}{2}$  per cent. Herreshoff patented<sup>1</sup> a device for reducing the amount of flue-dust formed in the descent of the charge. Some temperature measurements have been published by Clevenger.<sup>2</sup>

The improved Herreshoff Furnace, 20 ft. inner diameter and six roasting and one drying hearths, installed at Clifton and Douglas, Ariz., is shown in vertical section<sup>3</sup> in Fig. 67. The  $\frac{5}{8}$ -in. boiler-iron shell is lined with 8-in. fire-brick. The hearths have a spring of arch of 10.5 in.; they are built of 6- and 8-in. fire-brick, and furnish thus a support for the loose bottom on which the ore travels. At the periphery of an odd-numbered hearth are 54 drop-holes 18 by 14 in. An even-numbered hearth has a central discharge on an 8-ft. circle; the central shaft is 42 in. in diameter. The top hearth has four doors, the other hearths have six each.

The central hollow cast-iron shaft is made in three sections connected by

<sup>1</sup> U. S. Patent, No. 729,170, May 26, 1903.

<sup>2</sup> *Met. Chem. Eng.*, 1913, XI, 448.

<sup>3</sup> *Min. Sc. Press*, 1913, CVII, 683; *Eng. Min. J.*, 1914, XCVII, 262.

tongue and groove joints; bolt-heads and nuts are protected by pockets filled with refractory material. The hollow rabble-arms are similarly connected with the shaft. Inside the 42-in. shaft is an 18-in. steel tube to which are bolted pipes (not shown) reaching into the rabble-arms. Air is forced into the tube at the bottom (5500 cu. ft. per minute at 1.75 oz. pressure), it passes outward

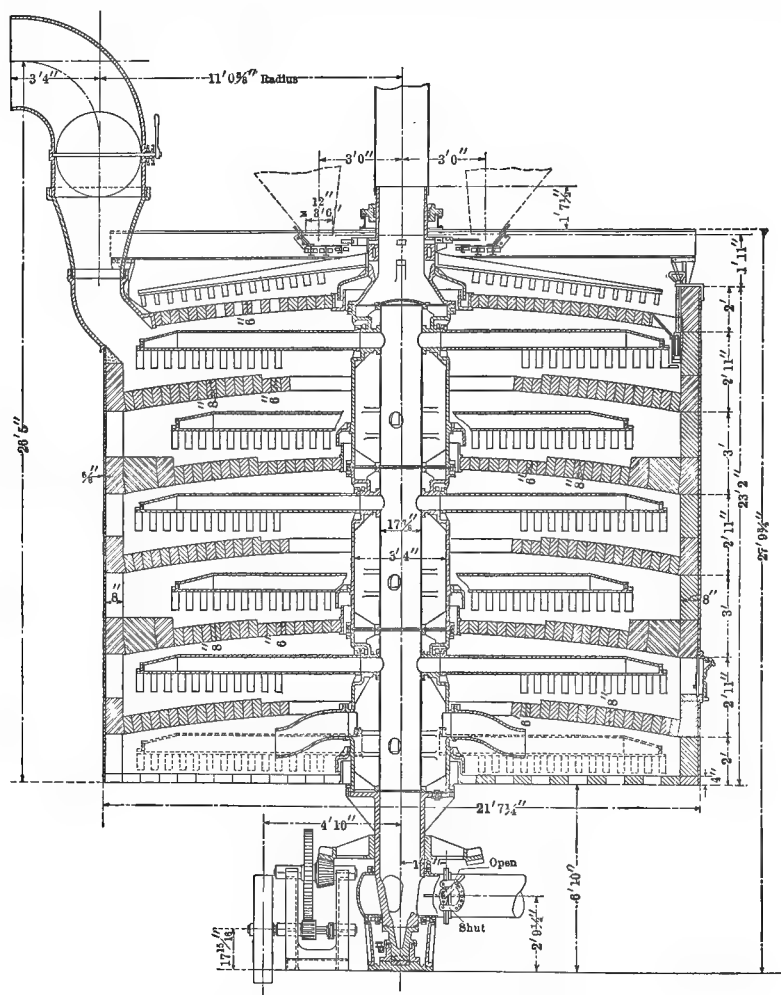


FIG. 67.—Herreshoff furnace, improved form.

in the pipes to the ends of the arms, returns between pipes and arms, and is either delivered as warmed air on to the bottom hearth or passes off at the top. The manner of attaching the rabble-blades to an arm is shown in Fig. 68. In some furnaces a hollow rabble-arm has a vertical partition extending to near the end, so that the cooling-air passes outward in one compartment and returns in the other.

The ore is discharged from the feed-hopper on to the top hearth mechanically by a passing arm which makes 60 r.p.m. The space between the top of the furnace and the central shaft is sealed with sand; in the furnace calcined material replaces the sand. Part of the dust carried away by the gases is collected by a hopper which discharges on to one of the lower hearths. The same arrangement is found at Hayden, Ariz. It is expected that a furnace will rough-roast in 24 hr. about 80 tons of copper-bearing concentrate.

At the works of the General Chemical Co., Edgewater, N. J.,<sup>1</sup> a 16-ft. furnace roasts in 24 hr. 5-6 tons Spanish pyrite reducing the S-content from 46 to 0.5 per cent. At this plant it takes from five to six days to exchange a broken rabble-arm, as the furnace has to be cooled down slowly and sufficiently to allow a man to enter and make the repair.

In another Eastern sulphuric-acid plant the cooling air is introduced at the top of the central shaft, admitted on to the hearths through the rabble-arms, and the sulphurous gas drawn off near the bottom. The claim made is that by this means the desulphurization is carried farther than when the air travels upward, and that the amount of flue-dust formed is greatly diminished.

**68. The O'Brien Furnace.**<sup>2</sup>—Fig. 69 gives a side elevation of a six-hearth furnace with mechanical screw-feed placed on a drying floor 6 ft. above the top of the furnace; the same feeding apparatus for dry ore placed on the furnace is indicated by dotted lines. To the right are seen the single gas-outlet and six doors; there are twelve in all, two for each hearth. The leading characteristics of the furnace are the air-cooling and the attachment of the rabble-arms, both shown in Figs. 70-72. The hollow built-up, cast-iron driving-shaft, tapering from top to bottom, has two vertical  $\frac{3}{4}$ -in. ribs making three compartments, a central *c*, for cold-air inlet, and two laterals, *d*, for hot-air outlet. It further has for each hearth two sockets, *e*, to receive the conical ends of the rabbling arms, which are locked in place by rib *b*, and socket *a*. On the lower inner side of socket *e*, is the opening *f*, for admission of cold air (natural or forced draft) from the central compartment *c*. The air travels outward in the rabbling arm under the horizontal partition *m*, returns above the latter, and leaves the arm through port *g*, into the hot-air compartment *d*. Putting in and taking out the arms horizontally permits diminishing the distance between hearths and having therefore a larger number of hearths or a greater hearth area for a given height than ordinarily; thus an O'Brien kiln with six hearths is only 13 ft.  $2\frac{1}{4}$  in. high, outside. In Fig. 69 the central shaft, running on ball-bearings

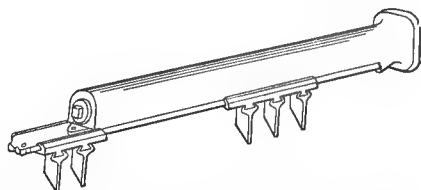


FIG. 68.—Rabble-arm and blades of improved Herreshoff furnace.

<sup>1</sup> Illustration, *Eng. Min. J.*, 1914, xcvi, 262.

<sup>2</sup> American Coke and Gas Construction Co., Camden, N. J. *Falding, Min. Ind.*, 1900, ix, 623.

Editor, *Iron Trade Rev.*, April 20, 1905, p. 56.

held in adjustable supports, is seen to be driven from below by means of a flexible plate, *n*, of large diameter, with steel rack driven by means of pinion *o*. In case any obstruction hinders the circuit of a rabble-arm, the plate jumps out of mesh, and the furnace comes to a standstill. Opposite pinion *o*, is a second pinion, *p*, through the shaft of which the screw-feed receives its motion by means of a sprocket wheel and chain.

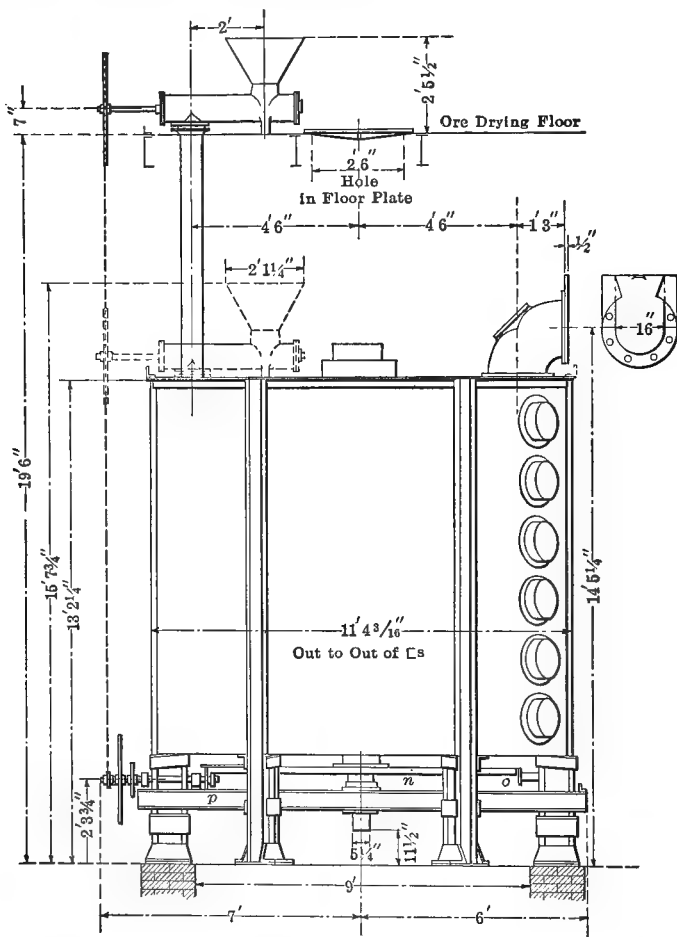


FIG. 69.—O'Brien furnace.

The rated capacity of this six-hearth furnace is 7000 lb. 45-per cent. free-burning pyrite; in practice the amount treated in 24 hr. has shown a range of from 5000 lb. 50-per cent. to 7500 lb. 40-per cent. pyrite when fairly free-burning.

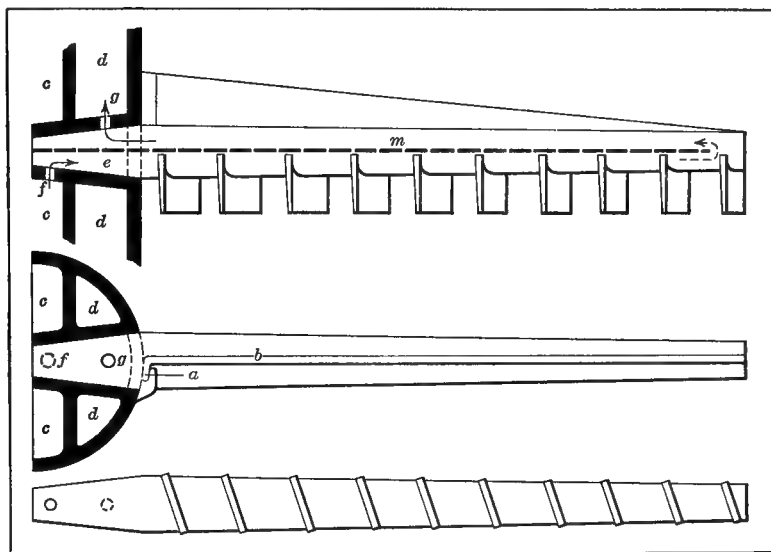
The following furnaces have become of some importance in the roasting of pyrite for the manufacture of  $H_2SO_4$ . The Kauffmann,<sup>1</sup> Herkules,<sup>2</sup> Heinze-

<sup>1</sup> Erzröstgesellschaft, Cologne, Germany.

<sup>2</sup> Dr. L. Lutjens, Chemist and Engineer, Hanover, Germany.

Freeland,<sup>1</sup> Merton,<sup>2</sup> the Sjöstedt<sup>3</sup> already quoted, and the Renwick<sup>4</sup> with a downward path of the gas current.

**67. The Evans-Klepetko Furnace of Great Falls.**<sup>5</sup>—The leading differences between this furnace and the two preceding are the size, the water-cooling of the central shaft and rabble-arms, and the form and attachment of the rabble-teeth. Figs. 73-76 give the details of the furnace, and Fig. 77 the general arrangement of building with two rows of furnaces at Great Falls, Mont.



FIGS. 70-72.—Rabble-arm of O'Brien furnace.

The furnace, Fig. 73, *a-d*, is a vertical cylinder of  $\frac{3}{8}$ -in. boiler iron, 18 ft.  $3\frac{1}{2}$  in. high by 15 ft. 10 in. in diameter, lined with a full course of red brick; it stands on columns, *a*, 12 ft. high, to allow the roasted ore to be collected in hoppers, *b*, and thence discharged into cars. The kiln is divided into six roasting chambers or floors by brick arches, with a 9-in. spring, that are 3 ft. apart and have for the passage of ore and gases annular openings, *c*, on the odd-numbered, and peripheral ones, *c'*, six to a floor, on the even-numbered hearths. The outer half of

<sup>1</sup> Wedge Mechanical Furnace Co., 115 Chestnut St., Philadelphia, Pa.

<sup>2</sup> Merton Furnace Co., 62 London Wall, London, E. C.

<sup>3</sup> *J. Can. Min. Inst.*, 1904, VII, 480; Pyrite Engineering Co., Carthage, N. Y.

<sup>4</sup> *Met. Chem. Eng.*, 1911, IX, 156.

<sup>5</sup> Allis-Chalmers Co., Milwaukee, Wis.

Croasdale, *Pac. Coast Miner*, 1903, VII, 471.

Sörensen, *J. Canad. Min. Inst.*, 1903, VI, 306; *Canad. Min. Rev.*, 1903, XXII, 87.

Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 277; *Eng. Min. J.*, 1903, LXXVI, 122.

Austin, *Tr. A. I. M. E.*, 1906, XXXVII, 462.

Moore, *Eng. Min. J.*, 1910, LXXXIX, 1021.

At Tooele Smelter, *Min. World*, 1910, XXIII, 944.

Corwin-Rodgers, *Tr. A. I. M. E.*, 1913, XLVI, 383.

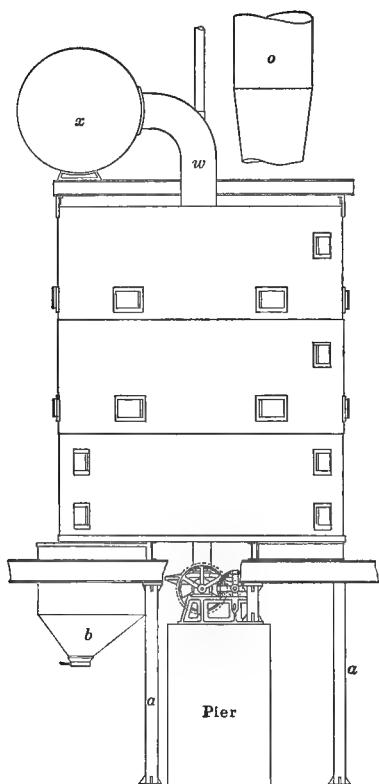


FIG. 73a. Elevation

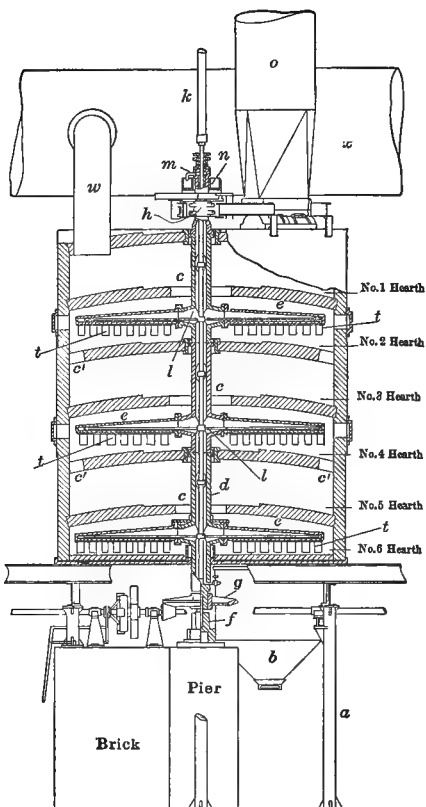


FIG. 73c. Vertical Section

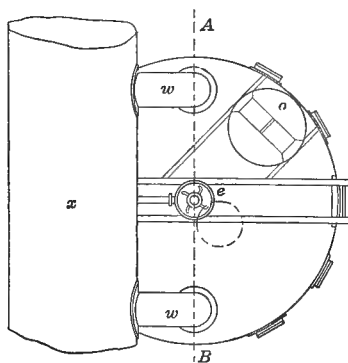


FIG. 73b. Plan

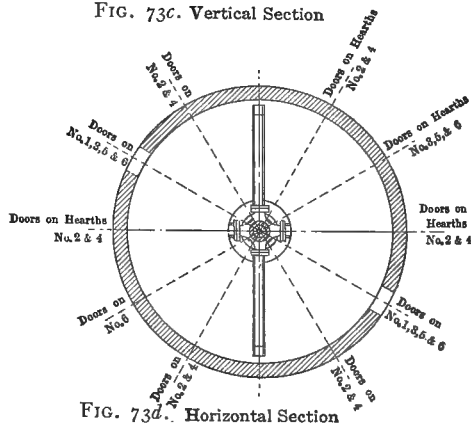


FIG. 73d. Horizontal Section

FIGS. 73a-d.—Evans-Klepetko furnace of Great Falls, Mont.

a hearth is 9 in. thick, the inner only 6 in., in order to reduce the weight at the center, to prevent contact with rabble-teeth when the hearth rises upon heating, and to furnish an offset for holding in place and horizontal the loose working-bottom (crushed limestone) which is 4 in. thick at the center and 9 in. at the periphery. In the center is the hollow, built-up, cast-iron driving-shaft, *d*, 9 in. inner diameter, to which are bolted opposite, hollow, cast-iron rabble-arms, *e*, two to each hearth, the arms of one hearth being set at 90 deg. to that of the other.<sup>1</sup> Copper gaskets are used to make the joints water-tight. The shaft extends through the bottom and top of the furnace, is carried by foot-step bearing *f*, and driven from below at the rate of 38–60 r.p.h. by bevel gear *g*; it is supported at the top in a journal-box, *h*, and carries a gear-wheel *i* (Fig. 75), which drives the mechanical feeder. The cooling-water from tank *j* (Fig. 77) is received in 6-in. pipe *k*, (Fig. 72), extending upward vertically about 8 ft.

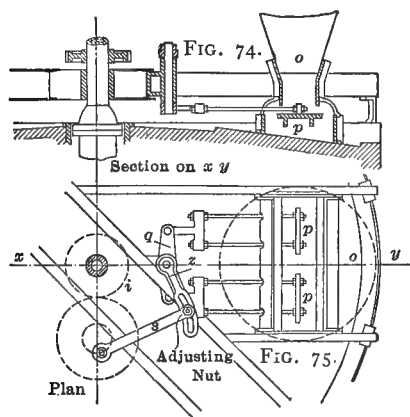


Fig. 76. Rabble-arm and teeth

FIGS. 74–76.—Evans-Klepetko furnace of Great Falls, Mont.

above the central shaft; it is then reduced to 3 in., extends downward toward the bottom of the driving-shaft, and has branches *l*, leading almost to the ends of the rabble-arms. The cooling-water thus flows through a 3-in. stationary pipe toward the bottom of the revolving shaft, and toward the ends of the stirring-arms through 1-in. pipes. In its upward passage between shaft and pipe it takes up the return-water from the arms and discharges at the top through 2 or 4 spouts *m* (Fig. 72) into a stationary launder, *n*. About 20 gal. cooling-water are required per minute with the overflow-water at 80° C.

A furnace has two 33-ton feed-hoppers, *o*, covered with a grating to keep out lumps; they are 10 ft. apart, 4 ft. 6 in. in diameter for 9 ft. 6 in., and then conical for 7 ft. 6 in.; at the bottom they are 3 ft. 6 in. by 1 ft. 2 in. (the cross-section of the opening in the roof of the furnace). The weight of the ore-column pressing downward prevents any hanging of wet concentrate. The contents of the hoppers are discharged continuously by two bars, *p* (Figs. 74–75), passing to and fro under the mouth with a throw of 10 in.; the rods of the feeders are joined to a

<sup>1</sup> Klepetko has patented (U. S. Pat. No. 744,359, Nov. 17, 1903) the use of three arms on each hearth; two arms are simply to stir the ore, the third is to move it.

cross-piece, *q*, which is pivoted in the center and connected by a rod to one end of a link, *z*, while the other is attached to the pitman, *s*, of a crank and spurwheel, the latter being geared to the central shaft of the furnace.

The ore is spread on the top hearth to a thickness of 3–3.5 in. The tops of the rabble-arms are protected by cast-iron caps against rapid wear at the places where the ore-column comes down through the feed-openings. The two arms of a hearth have 7 and 8 cast-iron teeth, *t*, 8 in. long by 6 in. wide by  $\frac{5}{8}$  in. thick;

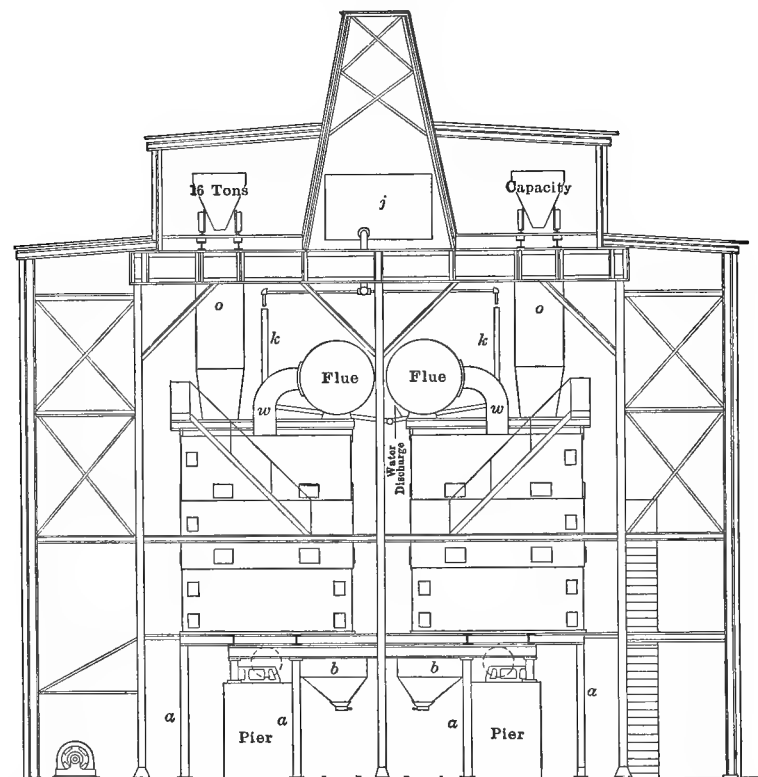


FIG. 77.—General arrangement of building with Evans-Klepetko furnaces at Great Falls, Mont.

the lower 3 in. which come in contact with the ore are chilled. The teeth (Fig. 76) have grooved collars, *u*, fitting over ribs, *v*, in the arms, and are slipped over the latter. As the teeth wear off, the ore builds on the loose working-bed; when they are to be replaced, a plow is first slipped over the rabble-arm and moved a little toward the center after every circuit in order to break up and bring to the surface any crust that had been formed. The teeth on the top hearth last one month, those on the bottom hearth seven months, the difference being due to wear caused by decrepitation; on the hottest hearths, the fourth and fifth, the teeth are attacked by the ore, thus, at Anaconda, pyrrhotite and chalcopyrite, hardly existing in the ore, formed on the teeth.



**GASES.**—The gases,<sup>1</sup> having the composition  $\text{SO}_2$  2.25,  $\text{SO}_3$  0.53, O 18.45, N 78.77 per cent. vol., and a temperature of about  $315^\circ\text{C}$ ., pass off through two gas-flues, *w*, 2 ft. in diameter and 12 ft. apart, ending in a main, *x*, 6–7 ft. in diameter for three furnaces; this is provided with discharge-hoppers for removing flue-dust, which amounts to 4–6 per cent. of the weight of ore treated. The sheet-iron uptakes have been replaced by brickwork at Garfield,<sup>2</sup> as the iron was quickly corroded.

**FURNACE BATTERY.**—From six to eight furnaces form a battery. They are placed 18 ft. apart from center to center in one direction, and 21 ft. 3 in. in the other. Three or four furnaces receive their motion from one main shaft, with which they are connected by friction clutches; 10 h.p. is required by six furnaces.

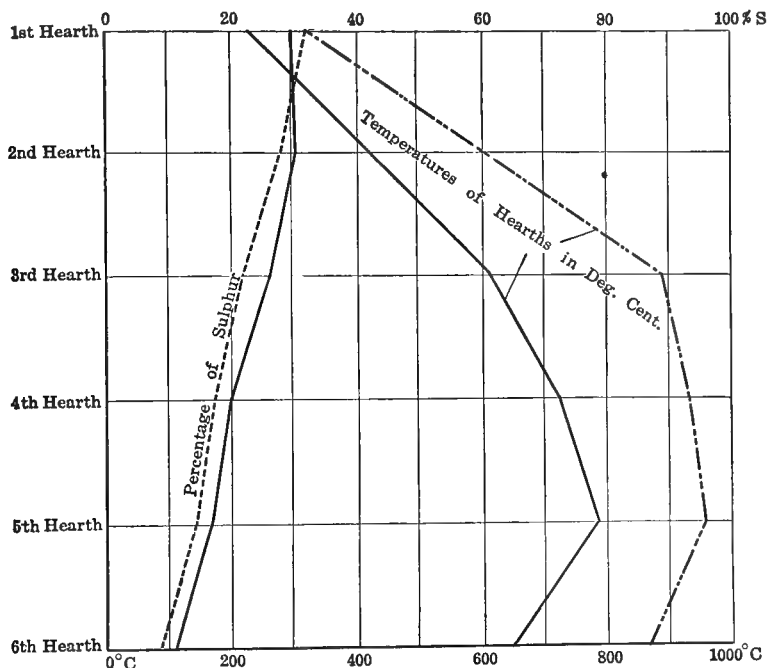


FIG. 78.—Changes of temperatures and sulphur-contents in two Evans-Klepetko furnaces.

The cost<sup>3</sup> of a furnace is given as being from \$5 to \$6 per square foot of hearth area. The necessary draft for four furnaces is supplied by a lined steel stack, 200 ft. high, 20 ft. inner and 23 ft. 6 in. outer diameter.

**STARTING FURNACE.**—In starting a furnace, crushed limestone is fed to form the working bottom. A fire of dry long-flame wood is started from the three side-doors of the third and fifth hearths, is kept going for two days with an old, and for three to four days with a new furnace, when the walls will have been

<sup>1</sup> Austin, *op. cit.*, p. 468.

<sup>2</sup> Moore, *op. cit.*, p. 1023.

<sup>3</sup> Editor, *Eng. Min. J.*, 1906 LXXXII, 226.

brought to a dark red. Concentrate averaging perhaps 25 per cent.  $\text{H}_2\text{O}$  is now fed; roasting begins on the second or third hearth, depending upon the strength of the draft (normal depression 0.3 in. water) and the number of circuits of the arms (normal 1 rev. in 60 sec.). Usually a blue flame is seen near the periphery of the second hearth; sparks become visible on the third; they cease on the fourth; the highest temperature is reached on the fifth. Changes in S-content and in temperature of two separate cases recorded by Austin and Croasdale are given in Fig. 78.

**TEMPERATURE.**—The temperature can be reduced either by opening doors on the third hearth and thus checking the draft, or by feeding more low-S material (fourth-class ore screenings, slimes), than normally; it is increased by accelerating the machinery and by feeding more coarse ore or high-S material than normally. Usually, however, the speed of the arms and the rate of feed, and with it the tonnage and the character of the roast, are kept constant so as not to interfere with the subsequent smelting in the reverberatory furnace.

The ore-charge passes through the furnace in about 90 minutes, the necessary air being admitted through the three doors on the bottom hearth. While the ore drops from hearth to hearth, the upward gas-current carries with it dust which striking the roof adheres to it in part and forms crusts. In the same manner the ports become incrustated. The different parts of the furnace where the ore is found to stick are sometimes lined with cast-iron plates to facilitate removing the crusts; these form a welcome blast-furnace ore, especially as they run lower in  $\text{SiO}_2$  than the calcine, *e.g.*, 6 *vs.* 30 per cent.  $\text{SiO}_2$ . The dust, from 4 to 6 per cent. of the weight of the ore depending upon the size treated, is richer in S than the ore.

**CAPACITY.**—A furnace treats, in 24 hr., 40 tons of Montana concentrate, (with S 35 per cent., Cu 10 per cent.) or 84 lb. per square foot hearth area, reducing the S-content to 7 per cent.; a greater reduction causes the formation of  $\text{Fe}_3\text{O}_4$ , and this makes trouble in the subsequent smelting.

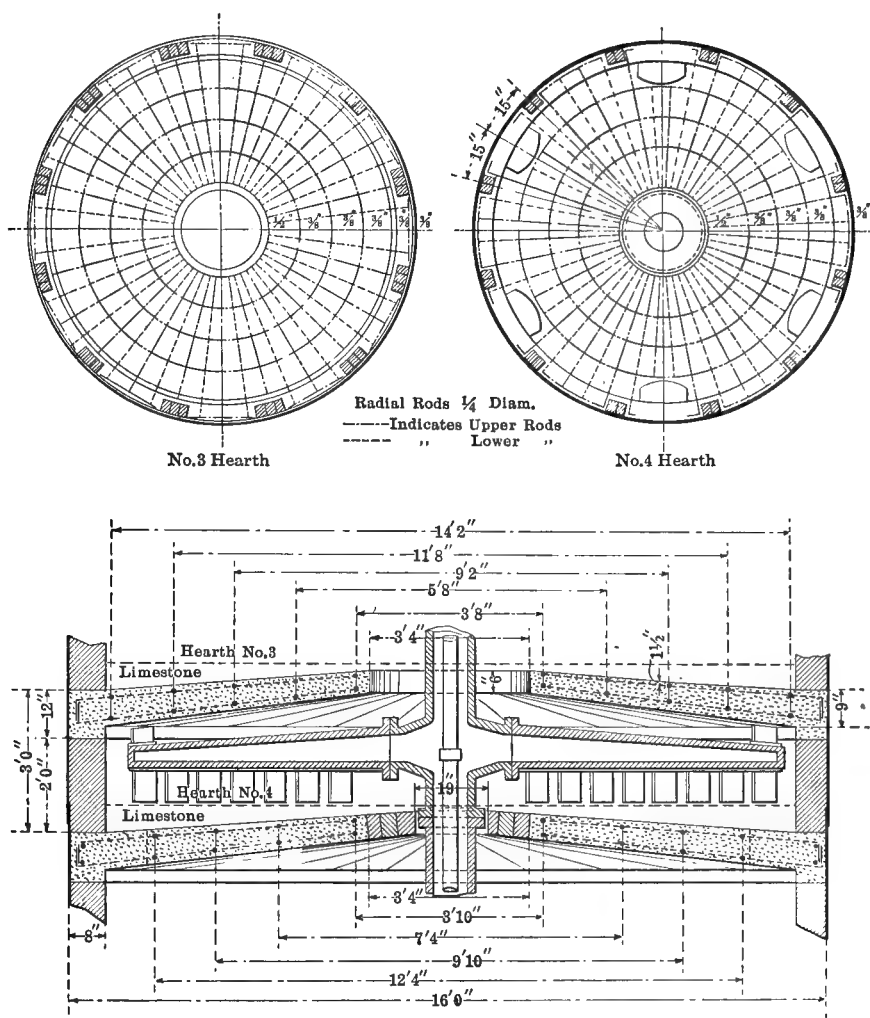
**IMPROVEMENTS.**—Since 1894 some changes have been made at Great Falls in the details of construction and in the mode of operating which have resulted in a simplification of the rabble-arms, a strengthening of the hearth, an increase in tonnage without materially raising the S-content of the calcine, and a decrease in the amount of flue-dust formed.<sup>1</sup>

At present the rabble-arms in the first hearth have no water-cooling whatever, as this has been found to be unnecessary; further, the 1-in. branch-pipes (*l*, Fig. 72) delivering cooling-water from the vertical 3-in. supply-pipe to the ends of the other rabble-arms have been removed, as incrustations of lime or oxide of iron, and suspended mud are likely to choke them.

**CEMENT HEARTH.**—The hearths since 1912 have been built of cement concrete instead of brickwork. The experience with this change has been satisfactory (May, 1913), as the hearths show no cracks, no wear, and incrustations are readily removed from the smooth surface. A concrete hearth, Figs. 79-81, made of 1 part Portland cement, 2 parts tailings sand, and 4 parts crushed slag,

<sup>1</sup> Corwin and Rodgers, *Tr. A. I. M. E.*, 1913, XLVI, 383.

is reinforced by two pair of concentric iron rings, each tied by 24 radiating 0.25-in. iron rods; one pair is placed 1.5 in. below the top, the other 1.5 in. above the bottom of the concrete; the inner ring is a 0.5-in. iron rod, the outer a  $\frac{3}{8}$ -in. rod.

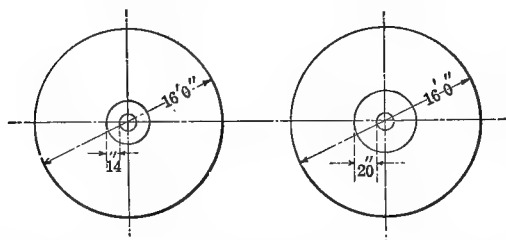


FIGS. 79-81.—Concrete hearth in Evans-Klepetko furnace of Great Falls, Mont.

**INCREASED DRAFT.**—The first experiments made in 1906 to raise the tonnage of a furnace by increasing the draft were successful. Strengthening the draft without feeding more ore caused the furnace first to grow cool and then to go out. By raising the draft from a water-depression at the furnace of 0.139 to 0.93 in., the tonnage could be increased from 36.1 to 45.7 tons without any change in the percentage of S; the S-content of the calcine became too high

when the feed was increased to 50 tons per day. This increased tonnage caused the center drop-hole in the third hearth to become more incrustated than usually; the hole, 14 in. wide, Figs. 82-83, of one furnace incrustated more quickly than that of another furnace where it was 20 in. wide; in fact 7 per cent. more time was lost with it in barring, etc., than with the larger hole. This shows that either the distance of 14 in. must be increased to 20 in., or additional drop-holes provided. Enlarging the central hole caused the S-content in the calcine to become higher than desirable; the alternative is the present practice; the third hearth, Fig 86, has a 14-in. central drop-hole and two extra drop-holes, 6×7 in., close to the edge of the central hole. The inner blades of the rabble-arm in

the third hearth, one to an arm, are set to push the ore away from the center so that most of the ore is dropped at intervals through the two extra drop-holes instead of being showered continuously through the center-hole.



FIGS. 82-83.—Center drop-holes, 14 and 18 inches wide, in Evans-Klepetsko furnace of Great Falls, Mont.

SPEED OF REVOLUTION.—A third factor in the roasting power of a furnace is the speed

of revolution of the central shaft. A high speed keeps the ore-bed shallow and counteracts the banking of ore in front of the rabble-arms; that speed is best which exposes a new surface to the air as soon as the rapid oxidation of an old one begins to cease. Thus the old speed of 1 rev. in 53 sec. has been abandoned; four furnaces have 1 rev. in 45 sec., and the others 18 have 1 rev. in 38 sec., with the result that the amount of charge treated in 24 hr. has been increased from 47.2 to 88.8 tons.

With an increased tonnage there is to be expected a rise in temperature. If this becomes excessive, it must be decreased by reducing the fuel value of the charge; this can be accomplished either by charging screenings from first-class ore ( $< \frac{1}{2}$  in.), or limestone required as flux, or both. Samples of roasting ore taken in 1911 gave upon analysis: Screenings, Cu 7.10,  $\text{SiO}_2$  46.9, FeO 16.6,  $\text{Al}_2\text{O}_3$  9.7, CaO 0.1, S 17.4 per cent.; and fine concentrate, Cu 7.45,  $\text{SiO}_2$  24.0, FeO 32.8,  $\text{Al}_2\text{O}_3$  6.1, CaO 0.1, S 33.4. On account of their low heat-value the screenings cannot be roasted by themselves without the use of extraneous fuel (coal or oil on the fifth hearth) even when air is blown into the fourth and fifth hearths from the sides or through radial perforated arms to hasten oxidation; in addition the drop-hole on the second hearth has to be narrowed to cause satisfactory ignition on this hearth.

As limestone remains unchanged in its passage through the furnace, it acts only as a diluent and not as a heat-absorbent; hence it is advantageously charged at the outer edge on the sixth hearth, where it becomes mixed with and warmed by the hot calcine. Its place is advantageously taken by screenings from first class ore. In this way the tonnage was increased in February 1913 to 105.08

tons charge (97.09 concentrate and 7.99 screening) with 11.6-13.1 per cent. S in the resulting calcine. Experience has shown that while the furnace can readily roast a 100-ton charge in 24 hr. with the central shaft making 1 rev. in 38 sec., the machinery cannot stand the strain. At present (record of April, 1913), the regular tonnage is 77.1 tons copper-bearing material with a reduction of the S-content in the calcine to 8.9 per cent.

**FLUE-DUST.**—The tests made to reduce the percentage of flue-dust were begun in 1911 by remodeling a furnace according to the device of Repath and Marcy<sup>1</sup> which provides separate ports for the passage of the ore and the gas. They showed that while the amount of flue-dust formed was reduced from 17.6 to 10.0 per cent., there took place with it a reduction in tonnage, 76.85 to 45.02 tons dry concentrate.<sup>2</sup>

**CROUSE EQUIPMENT.**—In 1912 tests were begun with the Crouse equipment, shown in Figs. 84-88, which carries the ore from the first hearth to the second, and from the second to the third through extra drop-holes, while the gas travels upward along its usual path. The extra drop-hole, 7×8 in., is situated about 4 in. from the center drop-hole; the two inner blades of the rabble-arm, one to an arm, push the ore away from the center toward the extra hole. The rabble-arms on the first, second, and third hearths are placed so as to be in line one above the other. The rabble-arm of the second hearth carries two iron boxes, open top and bottom, which extend from near the floor to close to the roof; the arrangement on the third hearth is similar. When a blade of an arm in the first hearth pushes the ore toward the extra drop-hole, the receiving box on the arm in the second hearth passes below the hole and protects the dropping ore from the gas-current. The same occurs when the ore from the second hearth drops through the side-holes on to the third hearth. The extra, 6×7 in., drop-holes on the third hearth permit using a 14-in. center-hole, Fig. 82, without incurring the trouble of heavy incrustation.

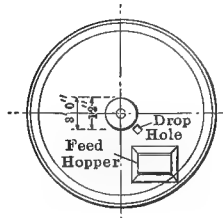
**SPARK CATCHER.**—The vertical section shows a spark-catcher on the fourth hearth. It consists of horizontal plates, which, extending in front of and in back of the ends of the arms, catch the sparks that are formed where the rabble-arm pushes the ore through the side drop-holes, and thus prevent the building of incrustations on the roofs.

The results of a five-day test showed that the regular furnace treated in 24 hr. 61.78 tons dry concentrate, reduced the S-content to 10.3 per cent. = 81.3 per cent. elimination, and made 17 per cent. flue-dust; the corresponding figures for the furnace with the Crouse equipment were 63.079 tons, 9.6 per cent. S, 81.2 per cent. elimination, and 10.7 per cent. flue-dust. Great Falls furnaces are being provided with the equipment.

**68. Evans-Klepetko Furnace at other Smelteries.**—This furnace was first built at Great Falls and has undergone modifications in various ways at copper smelteries to meet local conditions and to make the handling of ore and calcine

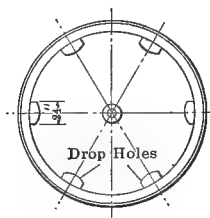
<sup>1</sup> Drawing in paper of Corwin and Rodgers.

<sup>2</sup> The paper by Corwin and Rodgers gives a method of determining the amount of flue-dust formed, without stopping the furnace.



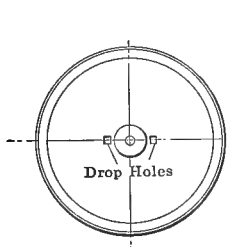
Hearth No. 1

The center drop hole is now used as a gas passageway only, and extra drop hole for concentrates.



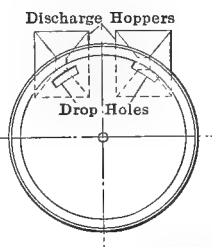
Hearths Nos. 2 and 4

Usually one or more of these side drop holes are covered to damp the air current.



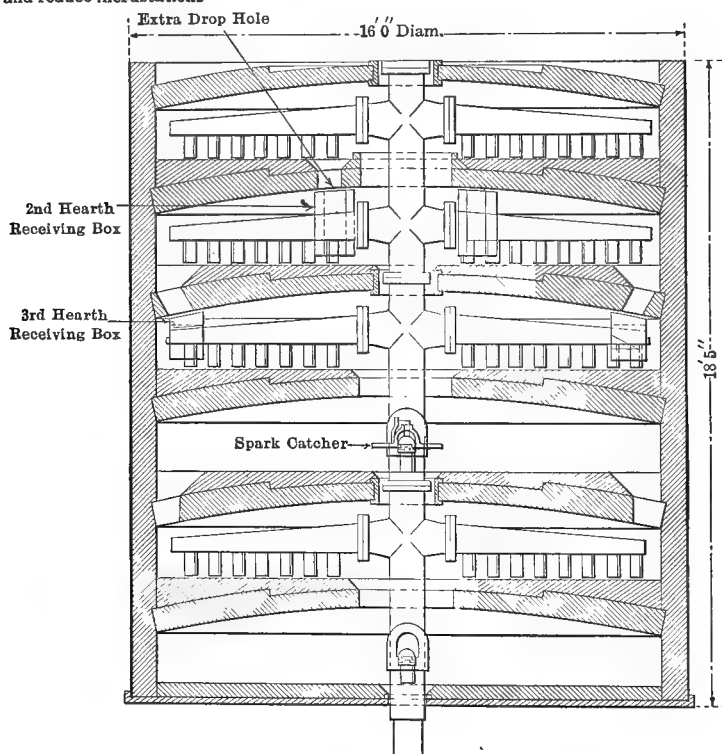
Hearth No. 3

The two extra drop holes through which the calcines fall to the hearth below, localize and reduce incrustations



Hearth No. 6

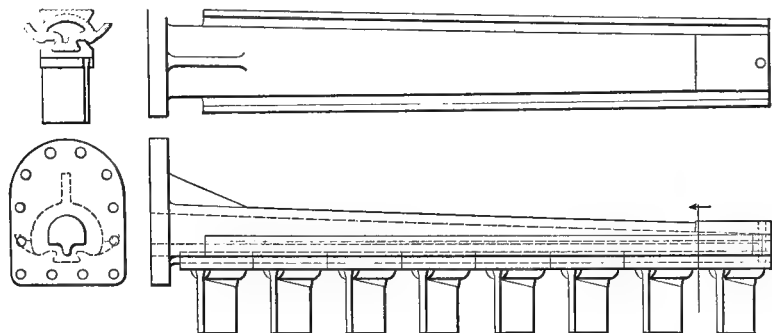
The discharge drop holes are 8 in. wide and 28 in. long on outer arc.



FIGS. 84-88.—Crouse equipment for dust-prevention in Evans-Klepetko furnace.

more and more mechanical. A few of the more important examples are given to illustrate the changes.

(1) THE WASHOE SMELTER, ANACONDA, MONT.<sup>1</sup>—The plant has 64 furnaces contained in a steel building, 96 by 142 ft. The furnaces are placed in 16 rows;



FIGS. 89-92.—Kelly-Thomson rabble-arm of Evans-Klepetko furnace at Anaconda, Mont.

each row of four receives its power from one main shaft; a steel structure with three working platforms embraces two rows of furnaces. The furnaces, placed 18 ft. apart in one direction and 21 ft. 3 in. in the other, are carried by steel frames 13 ft. 2 in. high. A furnace is 18 ft. 5 in. high outside and 16 ft.  $6\frac{1}{4}$  in. in diameter inside and 18 ft. outside, and has six hearths. The first, third, and fifth floors each have a center drop-hole, 16 in. wide, and three doors; the second and fourth floors have six side drop-holes, 18 in. wide, and the sixth hearth 2 side drop-holes, 14 in. wide, and four doors. The water-cooled shaft makes 1 rev. in 60 sec. The rabble used is the Kelly-Thomson<sup>2</sup> shown in Figs. 89-92. The 1-in. pipe which formerly delivered the cooling-water to the end of the arm, shown in Fig. 93, is omitted. In the ordinary arm, Fig. 93, the joint *A* becomes incrustated so that it is hard to remove the blade; further, leakages are not infrequent at this place. In the improved form, the joint of arm and blade is better protected against the calcine and is coated with tar; then the top of the arm is provided with ears which carry flue-dust and thus counteract the cooling-effect of the circulating water.

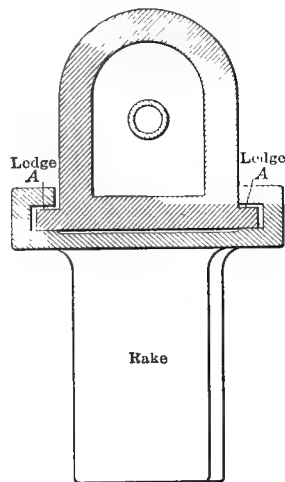


FIG. 93.—Original rabble-arm in Evans-Klepetko furnace at Anaconda, Mont.

The ore-charge is made up of 96-97 per cent. concentrate, 4-3 per cent. screening of first-class ore ( $< \frac{3}{8}$  in.), some MacDougall flue-dust (analysis below),

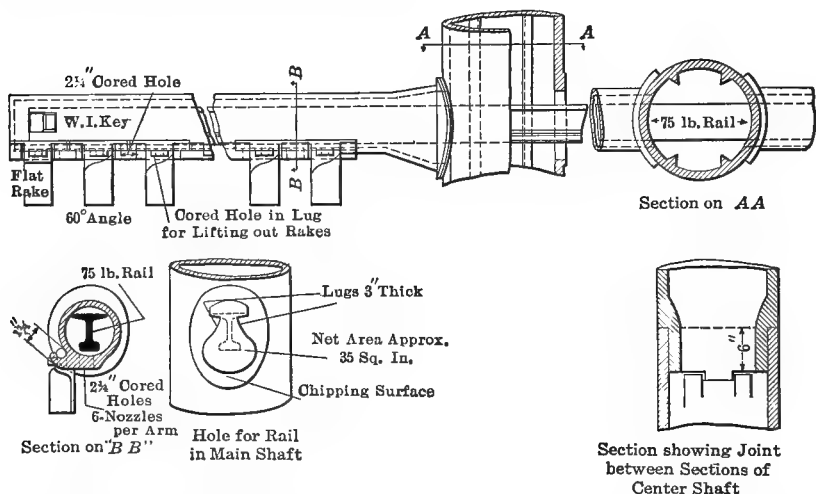
<sup>1</sup> *Tr. A. I. M. E.*, 1904, XXXIV, 258 (Hofman); 1906, XXXVII, 431 (Austin).

*Min. Ind.*, 1903, XII, 98; 1906, XV, 254 (Austin).

Peters "Practice of Copper Smelting," 1911, p. 78.

<sup>2</sup> *Eng. Min. J.*, 1911, XCI, 455.

and 3-5 per cent. limestone. The charge dumped from cars into the 33-ton feed-hoppers, passes in about  $3\frac{1}{2}$  hr. through the furnace. The furnace treats in 24 hr. about 40 tons charge assaying Cu 7-8 per cent. and S 32-33 per cent., reduces the latter to about 8 per cent.; has a draft of 0.5-0.6 in. water; requires 1.7 h. p. and 20 gal. water per minute with the overflow at 80° C. The loss in weight of the raw ore is about 18 per cent. A screen analysis of the calcine<sup>1</sup> gave, >10-mesh, 10 per cent.; 10- to 30-mesh, 25; 30- to 80-mesh, 50; <80-mesh, 35 per cent.; and a chemical analysis of a month's average sample, SiO<sub>2</sub> 27.7, FeO 39.0, CaO 2.4, S 8.0, Cu 8.66 per cent. A similar analysis of flue-dust showed SiO<sub>2</sub> 29.0, FeO 21.8, CaO 0.9, S 14.3, Cu 7.73 per cent. The 64 furnaces are attended in 24 hr. by 76 men; the cost of roasting is about 30 cents per ton with labor at \$3.00 for 8 hr.



FIGS. 94-98.—Shaft and rabble-arms of MacDougall furnace Steptoe Valley smelter.

(2) THE STEPTOE VALLEY SMELTER, MCGILL, NEV.<sup>2</sup>—There are 16 furnaces, which are 18 ft. in diameter and have six hearths. The floor of the first hearth is built of 1-in. cast-iron plates strengthened by 1-in. ribs, which hastens the drying of the concentrate containing about 10 per cent. water. The center shaft is air-cooled; air under a pressure of 2 in. enters at the bottom of the shaft and leaves through the arms. The construction of shaft and rabble-arms is shown in Figs. 94-98. The parts constituting the shaft are connected by bayonet couplings, one of which is shown in Figs. 94 and 95. The shaft, 16 in. in diameter, has oval openings for the rabble-arms, which have the form shown in Fig. 98; each of the two openings is provided with two 3-in. lugs, which carry a 75-lb. rail serving as support for the pair of arms of the hearth. The arms (Fig. 96), are slipped over the rail and wedged to its ends by wrought

<sup>1</sup> Offerhaus, *Eng. Min. J.*, 1908, LXXV, 1238.

<sup>2</sup> Sörensen, *Eng. Min. J.*, 1913, XCV, 1273.



iron keys and at the same time pressed against the flanges on the shaft. In this manner they are firmly connected with the shaft and can be readily removed when necessary. The cast-iron rabble-blades (Fig. 96 and 98), are provided with ears or trunnions by means of which they are suspended in hook-shaped lugs of the rabble-arm; a blade has a cored hole through which it can be lifted off the lugs.

The lack of S in the ore makes extraneous firing necessary. An oil-burner with a steam atomizer is used on the third hearth to ignite the ore. Roasting takes place mainly on the fourth and fifth hearths; often a flame is seen when the ore drops from the fifth to the sixth hearth.

The shaft makes 1 rev. in from 38 to 55 sec. The concentrate, which makes up the whole charge, assays Cu 10.6,  $\text{SiO}_2$  32.1, Fe 22.0,  $\text{Al}_2\text{O}_3$  5.0, S 24.7 per cent.; the calcine Cu 12.5,  $\text{SiO}_2$  31.9, Fe 25.7,  $\text{Al}_2\text{O}_3$  5.8, S 11.7 per cent. In 24 hr. a furnace treats 87 tons of dry concentrate (=90 tons wet), makes 2 per cent. flue-dust, consumes 27.4 lb. oil ( $14^\circ$  Bé and  $< 1$  per cent.  $\text{H}_2\text{O}$ ). The depression at the outlet-flue is only 0.07 in. water and the temperature  $260^\circ$  C. Limestone is not now fed with the ore nor on to the last hearth, as no advantage accrued from doing this. The 16 furnaces of the plant require in 24 hr. three foremen and 25.5 men excluding delivery of ore.

(3) THE GARFIELD SMELTER, GARFIELD, UTAH.<sup>1</sup>—There are in operation 14 furnaces with shells 19 ft. 6 in. in diameter and 16 with shells 18 ft. in diameter. The internal diameters are 18 ft. and 16 ft. 6 in. The central shaft and arms are air-cooled; each furnace is supplied with about 2000 cu. ft. air per minute at a pressure of 4 oz. The charge is delivered to the furnace by larry cars. It consists of concentrate varying in size from  $\frac{1}{4}$ -in. down to 200-mesh. The chemical analysis of an average charge is Cu 10,  $\text{SiO}_2$  24, Fe 21, CaO 6,  $\text{Al}_2\text{O}_3$  3, S 27 per cent. Additions of limestone are made on the fifth hearth. No extraneous fuel is used except in starting. An 18-ft. furnace puts through in 24 hr. 60 tons charge; a 19 ft. 6 in. furnace 70 tons. The calcine contains Cu 12 and S 10 per cent. There is made about 2 per cent. flue-dust. An average analysis of flue-dust shows: Cu 5.2,  $\text{SiO}_2$  30.3, Fe 6.6, S 3.5,  $\text{SO}_3$  30.5,  $\text{Al}_2\text{O}_3$  5.8, Pb 0.5, Zn 1.3, CaO 2.8, MgO 0.8, As 0.3. The draft in the roaster flue ranges between 0.25 and 0.30 in. water. The power required is 3 h.p.

(4) THE TOOEE SMELTER, TOOEE, UTAH.<sup>2</sup>—There are 32 furnaces arranged in four rows. They are 16 ft. inner diameter and have six hearths; on the third hearth is an auxiliary fire-place for starting the furnace when 1–2 per cent. fuel is mixed with the ore. The water-cooled central shaft takes 7500 gal. water in 24 hr. and makes 12 rev. in 60 sec. The charge, delivered by belt to hopper, is  $\frac{1}{2}$ -in. and smaller; it consists of pyrite with chalcopyrite, bornite, etc., in a siliceous gangue and contains as much as 10 per cent. sulphide copper concentrate. An average analysis shows Cu 3.56,  $\text{SiO}_2$  26.44, Fe 30.21, S 19.99,

<sup>1</sup> Private Notes, 1912; Private Communication, 1913.

<sup>2</sup> Thompson-Sicka, *Tr. A. I. M. E.*, 1913, XLVI.

Austin, *Min. Ind.*, 1911, XX, 235.

Private Notes, 1912; Private Communication, 1913.

CaO 4.36 per cent., Au 0.11 and Ag 1.5 oz. per ton. On the fifth hearth about 10 per cent. siliceous copper ore ( $\text{SiO}_2$  70–80 per cent., S none) is added. The draft in the discharge-flue is 0.2 in. water. A furnace roasts in 24 hr. 45 tons of charge; the calcine assays Cu 3.2 and S 7.4 per cent.; there is made 4.5 per cent. flue-dust with Cu 3.45,  $\text{SiO}_2$  26.0, Fe 26.0, S 13.5, CaO 6.0 per cent., Au 0.10 and Ag 1.85 oz. per ton. The power including line and countershafting and motor drives is 2 h.p. The labor for four furnaces per shaft is one furnaceman and one laborer.

(5) COPPER QUEEN SMELTERY, DOUGLAS, ARIZ.<sup>1</sup>—The new reverberatory-furnace division is laid out with 16 roasting furnaces placed in two rows. There are in operation nine air-cooled furnaces, 16 ft. inner diameter and six hearths. A furnace has three hoppers, two for ore and one for flux (limestone); an oil-burner is used in starting. The shaft makes 1 rev. in 60 sec. The concentrate to be roasted is assembled in 20 concrete bins, 16 ft. long by 15 ft. wide by 16 ft. deep, laid out in two divisions separated by the space taken up by the elevator; each division has two rows of five bins placed end to end, between which run surface-cars bringing in the concentrate. The bins are V-shaped, and closed at the bottom with 8- by 12-in. boards; they are discharged on to belt-conveyors, one for each row of five, the bottom boards being removed one after the other and replaced as soon as there is enough room. The belt-conveyors discharge into a pit from which the elevator delivers to bins above the roasting furnaces. The three furnace hoppers, holding together about 75 tons of material, are fed during the day from the bins alone by belts and trippers.

The chemical analysis of the ore shows Cu 13.9,  $\text{SiO}_2$  12.6, Fe 31.5,  $\text{Al}_2\text{O}_3$  3.6, S 34.0 per cent. Limestone is fed from the central hopper through an external pipe on to the fifth hearth; thus the reverberatory-furnace charge is made up in the roasting furnace. The draft is 0.5 in. water. A furnace treats in 24 hr. 50 tons of charge; the calcine contains Cu 15.8 and S 11.8 per cent.; there is made 4.5 per cent. flue-dust with Cu 13.6,  $\text{SiO}_2$  27.5, Fe 19.0, CaO 1.1,  $\text{Al}_2\text{O}_3$  6.6, and S 15.8 per cent.

The power required varies from 2 to 5 h.p. according to the condition of the furnace; the labor for eight furnaces per shift is one furnaceman and two helpers (one Mexican); the charging crew is separate.

(6) HAYDEN SMELTER, HAYDEN, ARIZ.<sup>2</sup>—There are in operation eight furnaces, arranged in a single row, 18 ft. and 21 ft. 9 in. in diameter; four furnaces have 5 hearths, and four 6 hearths; the center shaft is air-cooled. The charge consists of concentrates, which are delivered by belt-conveyors and trippers. A screen analysis of the concentrate shows: > 20 mesh 11.89 per cent.; 20–40 mesh 14.89; 40–80 mesh 17.21; 80–100 mesh, 11.82; 100–120 mesh, 14.95, < 120 mesh, 29.64 per cent. A partial chemical analysis gave Cu 18.75, S 23.2, Fe 21.6,  $\text{SiO}_2$  26.2 per cent. From 2 to 3 gal. California oil are burnt per ton of charge. A furnace puts through in 24 hr. from 90 to 100 tons of charge, which has a depth of from 6 to 8 in. The calcine assays Cu 19–21 per cent. and S 14–15

<sup>1</sup> Private Notes, July, 1912 and Communication, Aug., 1913.

<sup>2</sup> Private Notes, 1912; Private Communication, 1913.



per cent. The flue-dust collected in the hoppers of the roaster building amounts to about 0.75 per cent. of the charge; a partial analysis gave Cu 9.9, SiO<sub>2</sub> 52.8, Fe 7.8, S 6.3 per cent. The furnaces are run with a draft of 0.2 in. water. The eight furnaces require in 24 hr. six men to supply ore, and nine men for attendance.

(7) CANANEA SMELTER, CANANEA, MEXICO.<sup>1</sup>—There are in operation 10 furnaces (Figs. 99-111) arranged in two rows; a furnace has an inner diameter of 16 ft. 6 in. and six hearths. The center shaft is water-cooled with from 25 to 28 gal. water per minute. It makes 47 r.p.h. The charge is made up by bedding and reclaiming as are the blast-furnace charges (§ 177). The charge consists of concentrate (Cu 9.10, SiO<sub>2</sub> 19.6, Al<sub>2</sub>O<sub>3</sub> 4.5, Fe 26.5, CaO 1.3, S 29.0 per cent.) and siliceous flux. A furnace treats in 24 hr. 40 tons (dry) charge and burns 0.026 bbl. of oil per ton charge; the calcine assays Cu 10.83 and S 9.9 per cent.; there is made 6.54 per cent. flue-dust averaging Cu 9.01, SiO<sub>2</sub> 37.9, Al<sub>2</sub>O<sub>3</sub> 7.7, Fe 13.8, CaO 1.5, S 12.7 per cent. The draft is 0.45 in. water. The 10 furnaces are run by two 20 h.p. A. C. motors.

**69. The Wedge Furnace.**<sup>2</sup>—The leading features which distinguish this furnace, shown in Fig. 112, from the preceding Evans-Klepetko and its modifications are: a central accessible air-cooled driving shaft, 4 ft. in diameter, which without bottom-step runs on roller bearings; severally cooled rabble-arms which are removable through the central shaft; a large diameter (20 ft.) made feasible by the manner of support of the rabble-arms; a mechanically stirred drying-hearth for wet ore, which forms the top of the furnace.

The furnace, 21 ft. 7 in. in diameter outside and 27 ft. 5 in. high, has seven roasting-hearths and one drying-hearth. It is built of a ½-in. steel shell lined with a full course of red brick; the shell stands on columns 5 ft. 8½ in. high of structural steel to allow for automatic discharge of roasted ore into cars. The roofs are arched with a spring of 13 in., the floors are level, the hearths are 16 in. apart (2 ft. 9½ in. centers) and are built of special brick. Each hearth has the usual two rabble-arms, which make 1 rev. in 30 sec. The central driving shaft (53) is air-cooled, 4 ft. in diameter, of ½-in. steel plate, to which are riveted cast-iron furnace-arm holders (47); at the top it carries the dryer-arms (50). The furnace-arms (48) are provided with cast-steel breech blocks by means of which a man inside the shaft can loosen or fasten the holders. An exchange of arm including water connections is made inside of 30 min. The dryer-arms (50) are provided with adjustable plows (see below). The shaft (53) is supported by a master-gear (26) 12 ft. 3 in. in diameter, which is centered by a center pin (29) and provided with a cast-steel race-way (28) running on rollers (32) supported by pedestals (34). Power is derived from driving pulley (1) making 100 r.p.m., bevel gears (5 and 6), vertical intermediate shaft (16), worm and wormwheel (15), lower horizontal shaft (18), bevel pinion (23) (provided with safety-pin (25)), and master-gear (26). On top of the center shaft is the steel water-pan (42) supplying severally the cooling-water to the rabble-arms through lead pipes

<sup>1</sup> Private Notes, 1912; Private Communication, 1913.

<sup>2</sup> The Wedge Mechanical Furnace Co., 115 Chestnut Street, Philadelphia, Pa.

(54) provided with regulating-valves; the outlet pipes of the arms (55), as well as the overflow pipe from water-supply pan, end in a 4-in. cement water-receiving pan in the foundation, which has a 6-in. outlet. The hollow cast-iron rabble-arms

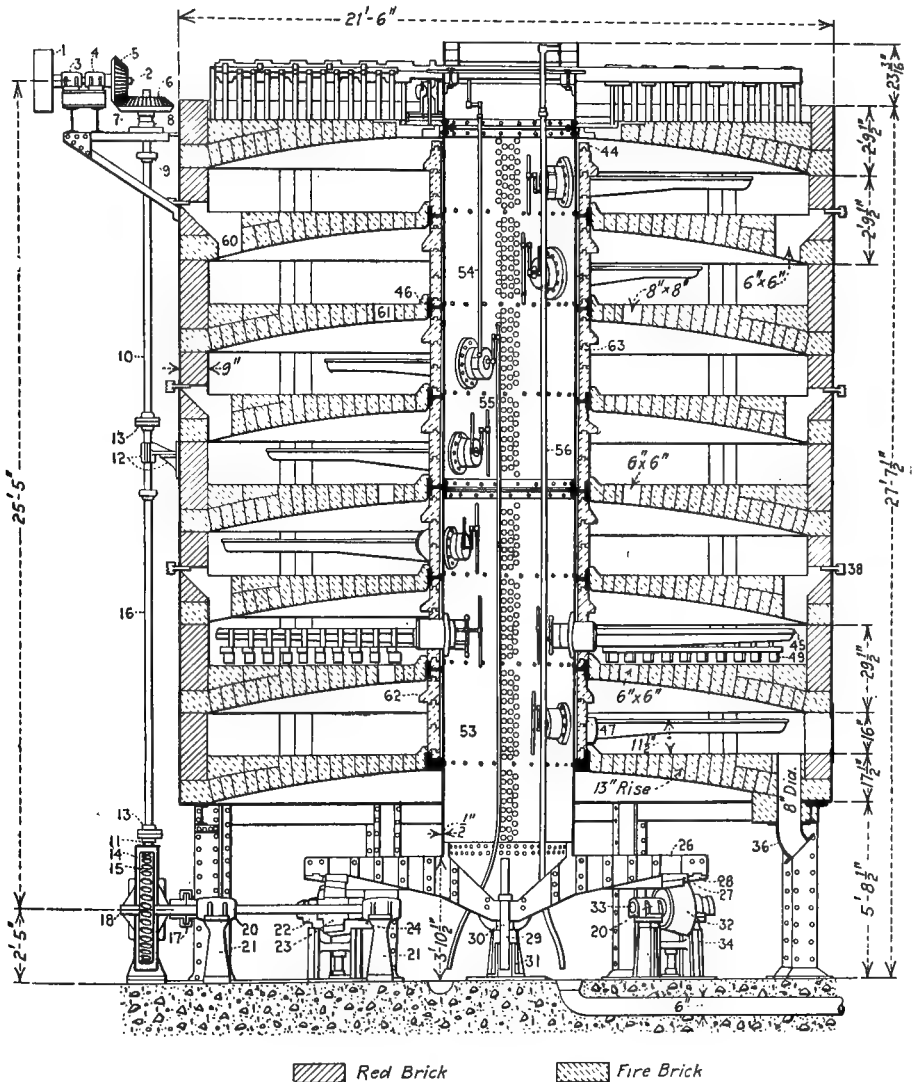


FIG. 112.—Wedge furnace.

(48) each have a central partition to enable the cooling-water to circulate; each furnace requires 32 gal. water per minute.

The rabble-arms are so placed that they are not touched by the ore dropping from hearth to hearth. They are provided with lifting blade-holders (45) and

blades (49) in order to prevent breakage of arms in case the blades strike any obstruction; a blade-holder is readily removed without stripping the arm, and the blade without disturbing the holder. The dryer-arm (50) is also provided with plow-holders (51); the plows are so secured to the holders that they can be lowered as they wear off; they do not drag on the hearth. The ore is fed by an elevator or belt to a 10-ton hopper (not shown) at the edge of the top of the furnace. The hopper has a rectangular discharge through which the ore drops on to the dryer-hearth, whence the plows of the dryer-arm move it gradually toward the center. There is a cast-iron feed-box (41) with removable feed-blades by means of which the amount fed to the furnace is regulated. The ore forms an air-tight seal and prevents the escape of any gas. Any large pieces not intended for the furnace cannot get into it, and are readily removed when noticed by the attendant. Drying the ore before feeding into the furnace has greatly reduced the formation of accretions, and keeps all moisture out of the dust-flues.

The furnace has a rectangular gas-flue (not shown) leading from the top hearth to the main flue. The bottom of the gas-flue is inclined in order to allow the flue-dust to glide downward to the cleaning doors in the side of the main flue. From 8 to 10 sq. ft. flue-area is required for a furnace; the power necessary is 2 h.p.; two men on a shift tend four furnaces.

This seven-hearth furnace, 20 ft. inside diameter, with a hearth area of 2381 sq. ft., treats in 24 hr. 100 tons sulphide copper ore with 35 per cent. S, reducing the S to 7 per cent., or 84 lb. per square foot hearth area. In Eastern sulphuric-acid works the capacity is from 16 to 20 tons pyrite with 50 per cent. S, roasting down to below 2 per cent. S, or 15 lb. per square foot hearth area.

The temperatures of a furnace, treating 100 tons sulphide copper ore with

TABLE 24.—TEMPERATURES IN WEDGE FURNACE

Hearth No.	1	2	3	4	5	6	7
Degrees C. ....	660	700	665	620	370	200	<260

29 per cent. S and 15 per cent. Cu, are given in Table 24. The temperature of the second hearth is the highest. In a sulphuric acid plant treating pyrite, the highest temperature (880° C.) is usually attained on the third hearth, while that of the seventh hearth falls to 150° C.

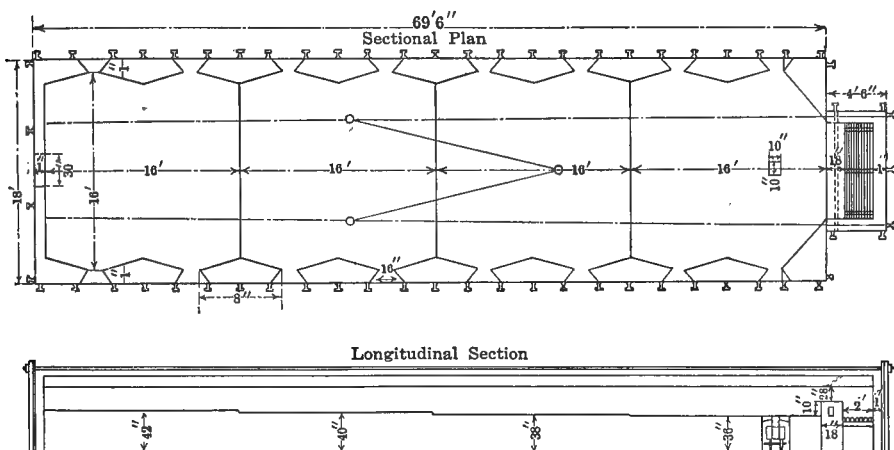
The cost of roasting in an Eastern acid plant with four furnaces treating 60 tons pyrite, in 24 hr., was in one instance \$0.18 per ton, *i.e.*, labor \$0.12, repairs 0.03, sundries 0.03.

At the new smeltery of the United Verde Co., Clarkdale, Ariz.,<sup>1</sup> six Wedge furnaces, 21 ft. 6 in. in diameter, with air-cooled rabble-arms have been installed; the air enters the arms under a pressure of 2 oz. The ore is brought from the storage-bins by belt-conveyors to the furnaces.

<sup>1</sup> *Eng. Min. J.*, 1913, xcvi, 289.

**70. Roasting in Reverberatory Furnaces.**—This form of furnace is suited for all sulphide copper ores that have been crushed to  $\frac{3}{16}$  or perhaps  $\frac{1}{4}$  in.; matte will have to be crushed more finely, say to  $\frac{1}{16}$  in. As the usual aim is to rough-roast only, reducing the S-content to about 7 per cent., the imperfectly roasted coarse and the overroasted fine particles will furnish a satisfactory average. The farther the expulsion of S is to be carried, the lower will have to be the limiting size of the ore, the more uniform the grain, and the slower the operation.

**71. The Single-hearth Hand Reverberatory Furnace.**—This form of furnace is little used at present for rough-roasting sulphide copper ore that is to be smelted. Horizontal and vertical sections of one form are given in Figs. 113 and 114.<sup>1</sup> A furnace with a hearth 60 by 16 ft. will roast in 24 hr. as much as 16 tons of free-burning pyritic ore, reducing the S-content from about 35 to 7 per cent.; this is equal to roasting 33 lb. ore per square foot hearth area.



FIGS. 113-114.—Single-hearth hand reverberatory roasting furnace.

In operating, 2 tons of raw ore are charged and their equivalent of roasted ore drawn every 3 hr. There are required two men in an 8-hr. shift and from 1 to 2 tons bituminous coal depending upon the quality, or 0.4 days labor and 0.094 ton coal per ton of raw ore. With ore that is not free-burning, the roasting capacity is smaller, perhaps 12 tons in 24 hr., the 2-ton charge being shifted every 4 hr.

The depth of ore-bed varies with the character of the ore from 2.5 to 4 in. Thus, *e.g.*, at the Parrot works,<sup>2</sup> a furnace 60 by 16 ft. treated in 24 hr. 10 tons concentrate, assaying from 16 to 40 per cent. Cu and about 35 per cent. S, in charges of 3600 lb., reducing the S-content to 7 per cent.; it consumed 2.25 cords of wood, and required four men.

At the Orford Copper Co.'s plant,<sup>3</sup> a furnace 60 by 12 ft. treated in 24 hr.

<sup>1</sup> Peters, "Modern Copper Smelting," 1895, p. 175.

<sup>2</sup> Peters, *Min. Res. U. S. Geol. Surv.*, 1883-84, p. 391.

<sup>3</sup> Howe, "Copper Smelting," p. 104.

12 tons matte, assaying from 40 to 50 per cent. Cu and 27 per cent. S, in 4000-lb. charges, reducing the S-content to 5 per cent.; it consumed 2 tons of coal and required eight men. The thickness of bed was 7 in. The amount of flue-dust formed in a hand reverberatory furnace is from 1 to 2 per cent.; the total cost of roasting in the western states is from \$1.50 to \$2.00 per ton.

The two-hearth furnace raked by hand is used only in very exceptional cases, when there is not room enough for one with a single hearth. While the hand reverberatory roasting furnace fulfils all the conditions necessary to obtain a satisfactory roast, the quantity of its product is small, as it is not possible to renew by hand-work the surface of the roasting ore with sufficient frequency to hasten the process in the required degree. The small capacity makes the cost high. Mechanical furnaces have therefore replaced most hand-furnaces for rough roasting.

**72. The Edwards Furnace.**<sup>1</sup>—This furnace was designed in Australia for dead-roasting gold ores previous to cyaniding. Its work has been so satisfactory that its field has been extended to rough-roasting sulphide and arsenical ores. Figs. 115-121, from drawings of the Stearns-Roger Mfg. Co., Denver, Colo., represent the Simplex Stationary Furnace. It is a single-hearth, straight-line, mechanical reverberatory furnace with a roasting hearth, *a*, 76 ft. 1½ in. long by 6 ft. 6 in. wide = 495 sq. ft.; it has an inclination from feed to discharge of 0.5 in. per foot, is heated from two fire-places, one, *b*, at the discharge-end, the other, *c*, at one side, 30 ft. 2 in. distant from *a*. On both sides are doors to furnish access to the rabblers and for admission of air. The ore, fed at *d*, is moved down the inclined hearth to the fire-place, *b*, where it is discharged through port *e*, into an underground passage, *e'*, containing an ore-car. The rabbling is accomplished by 21 revolving horizontal arms making from 1.5 to 2 r.p.m.; the arm nearest the feed, the feed-scraper *f*, is without teeth; the other arms each have four plow-shaped teeth, *g*. The arms, fastened to vertical spindles *h*, and *h'*, which pass through the roof, are held in position by iron frames *i* supported by the side-walls. Spindles *h'*, are water-cooled. All the spindles are rotated by bevel gears, *j*, meshing with bevel pinions, *j'*, on a single line-shaft, *k*, extending the length of the furnace. This carries at the center a spur gear, *m*, meshing with pinion, *n*, which is rotated through bevel gears, *o*, shaft, and pulley, *p*. The rotation of the spindles is such that each moves in the direction opposite to its immediate neighbor, causing the rabblers, which throw the ore outward, to move it in a zigzag course over the hearth, and to cover a path of from two to three times the length of the hearth. The circle of rotation of the outer end of one rabble-arm intersects that of its two neighbors; the only dead spaces are the triangles between the paths of the rabblers and the side-walls. The furnace construction requires 35,000 red brick and 3800 fire-brick. Operating requires 2 h.p. and one man per shift. The uniform rate of desulphurization of a sulphide copper ore attained at the Yampa smelter, Bingham Canyon, Utah,

<sup>1</sup> Simpson, *Tr. Inst. Min. Met.*, 1903-04, XIII, 27; *Eng. Min. J.*, 1903, LXXVI, 849. Warwick, *Min. Mag.*, 1905, XII, 196.

Metallurgist, *Min. Sc. Press*, 1910, CI, 50.



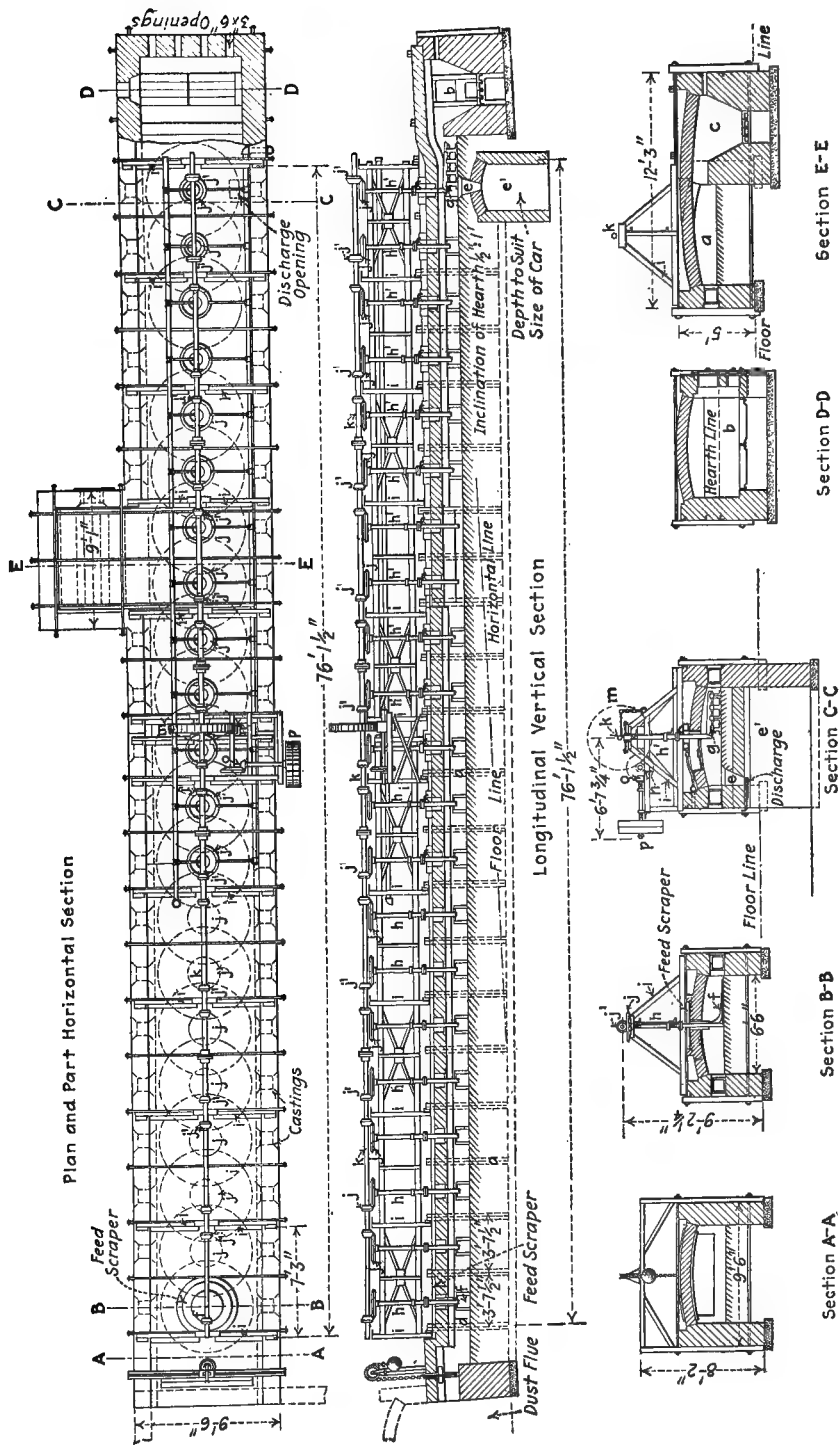


FIG. 115-121.—Edwards simplex stationary furnace.

in a duplex furnace, as given by Waring<sup>1</sup> and plotted by Austin,<sup>2</sup> is shown in Fig. 122.

Beside the furnace described, there are three other types in the market, the Duplex Stationary and the Tilting which is made either single or duplex.

A DUPLEX STATIONARY FURNACE is shown in vertical cross-section in Fig. 123, in which the parts similar to those in Figs. 115-121 have received the same designations. The hearth is 13 ft. wide and has two rows of rabblies; the latter are so distanced that there is an intersection of circles of rotation of the arms in each row, and no dead spaces exist along the center line of the furnace. The main details of the drawing are similar to those of Figs. 115-121.

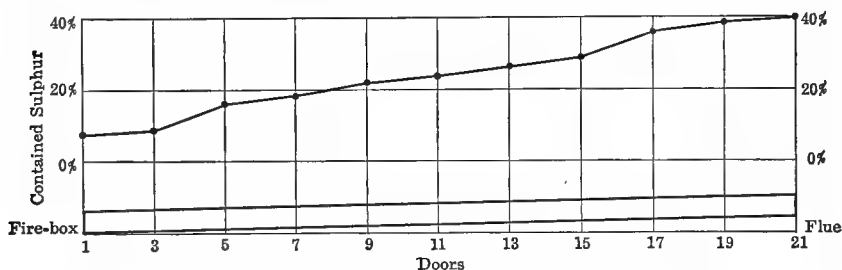


FIG. 122.—Desulphurization in Edwards simplex furnace.

The power for the rotation of the rabblies is derived from pulley *p*, the shaft of which carries at the opposite end a bevel pinion, *q*, meshing with bevel gear *r*; the shaft of the latter carries a spur pinion, *s*, meshing with spur gear *m*, and this drives through spur pinion *t*, the second spur gear *m'*.

With a fixed furnace the inclination, usually 1 in. per ft., is unchangeable; with the Tilting Furnace the angle can be changed with the character of the ore.

A TILTING FURNACE consists of two upright steel girders joined at the bottom and ends by a steel plate, and supported at the center, 2 ft. above the floor, by trunnions placed midway between the ends, while at one end there is a jack-screw for raising and lowering in order to give the hearth a slope suited to the required progress of the ore through the furnace. The iron work is connected in such a way that a furnace is readily dismantled.

The results obtained at the Yampa plant are given in Table 24.

TABLE 24.—WORK OF THE EDWARDS FURNACE AT THE YAMPA PLANT

	Simplex	Duplex
Hearth.....	6×57 ft.	11×92 ft.
Inclination.....	$\frac{1}{8}$ in. per ft.	$\frac{5}{8}$ in. per ft.
Spindles.....	2 r.p.m.	1 r.p.m.
Power.....	1 h.p.	4 h.p.
Capacity in 24 hr.....	25 tons	72 tons
S in raw ore.....	26-39 per cent.	
S in roasted ore.....	2.2-8.6 per cent.	
SO <sub>2</sub> in flue gases.....	4.3 per cent. vol.	

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Min. Ind.*, 1906, xv, 253.

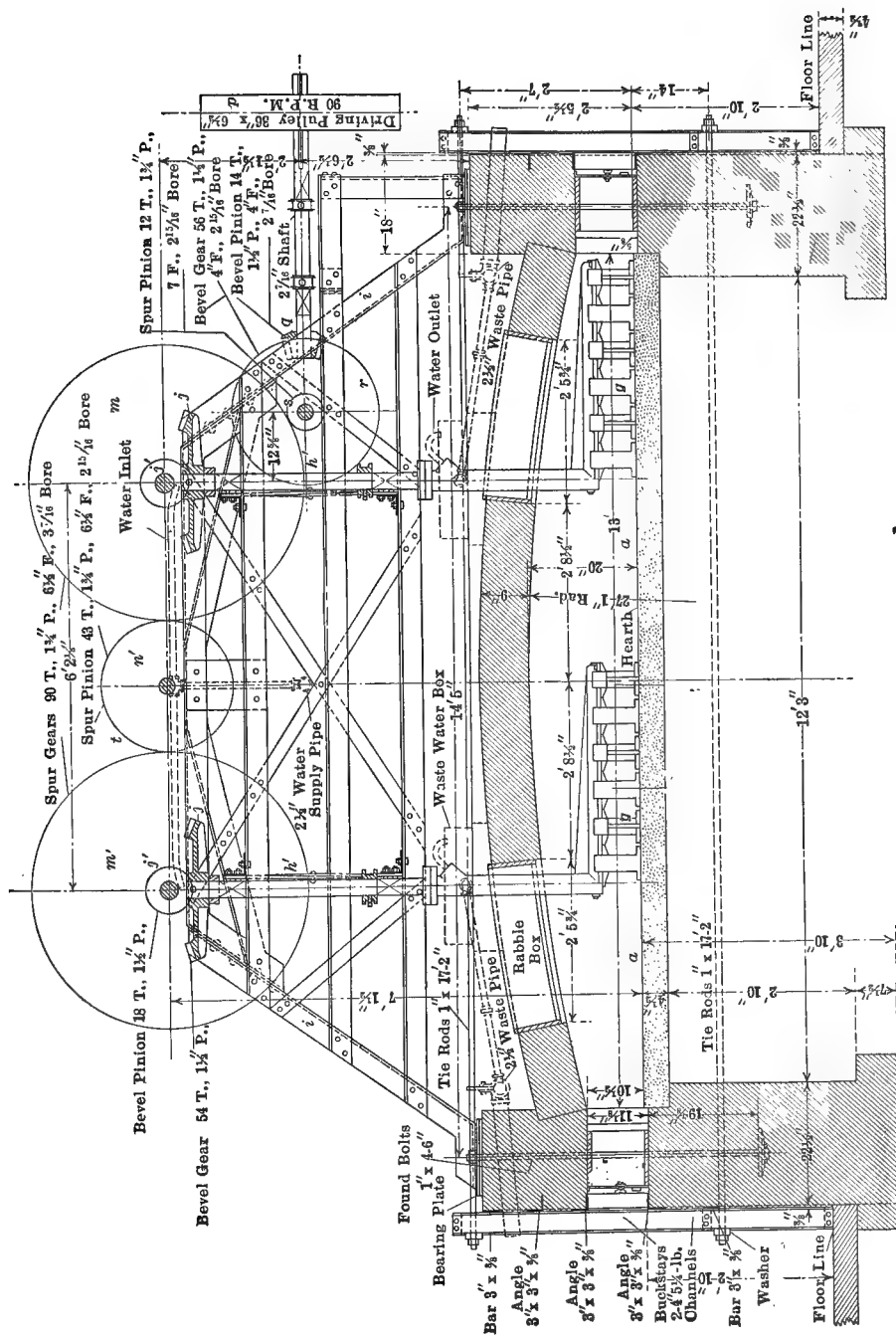


FIG. 123.—Edwards duplex stationary furnace; vertical cross-section.

Warwick<sup>1</sup> states that the capacity would be 15 per cent. greater if the draft were sufficiently strong. The furnaces have been replaced by MacDougall furnaces.

The works of the Consolidated Arizona Smelting Co., Humboldt, Ariz.,<sup>2</sup> have 3 duplex furnaces, 12 ft. by 91 ft. 10 in. with a total inclination of 36 in. The furnace is fired with 2 oil-burners, the coal fire-place 8 ft. by 2 ft. 4 in. serving as a combustion chamber; the furnace has 21 rabble-arms on a side, each with 6 teeth; 9 spindles are water-cooled; the 4 arms near the discharge make 4 r.p.m., the others 2. The copper ores treated are: a heavy dense pyrite crushed to 0.75 in. (Insol. 8, Fe 38, S 40 per cent.), a friable schistose pyrite (Insol. 50, Fe 15, S 18 per cent.), and a fine concentrate (Insol. 45, Fe 18, S 18 per cent.). One furnace treats in 24 hr. 50–60 tons mixture with 27 per cent. S, reducing this to 4–5 per cent., and makes 2–3 per cent. flue-dust; it consumes 250 gal. California crude oil per shift. One man and helper in an 8-hr. shift tend three furnaces; power is furnished by a 40-h.p. alternating-current motor; 50 gal. cup grease per month are used with the three furnaces and the transmission lines.

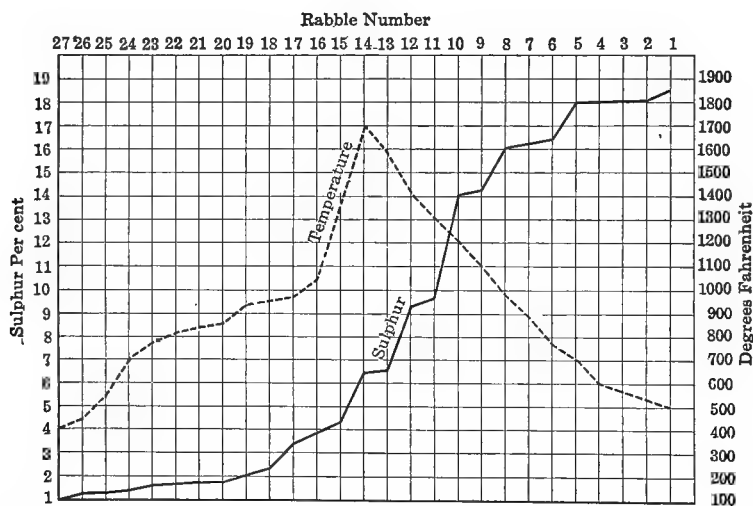


FIG. 124.—Changes of temperature and sulphur-content in Edwards duplex furnace

At the Goldfield Consolidated Mill<sup>3</sup> a furnace 112 by 13 ft. with two rows of 27 rabbles making 2.25 and two finishing rabbles making 4.8 r.p.m. roast dead in 24 hr. 40 tons concentrate ( $\text{SiO}_2$  51.60, Fe 19.90, S 18.93,  $\text{Al}_2\text{O}_3$  2.00, CaO 0.20, MgO 0.10, Sb 0.08, Se and Te 0.46, Cu 0.50) containing 10 per cent. water. The elimination of S in the furnace and the temperatures observed at the rabbles are shown in Fig. 124. The S begins to burn at the seventh rabble, and burns

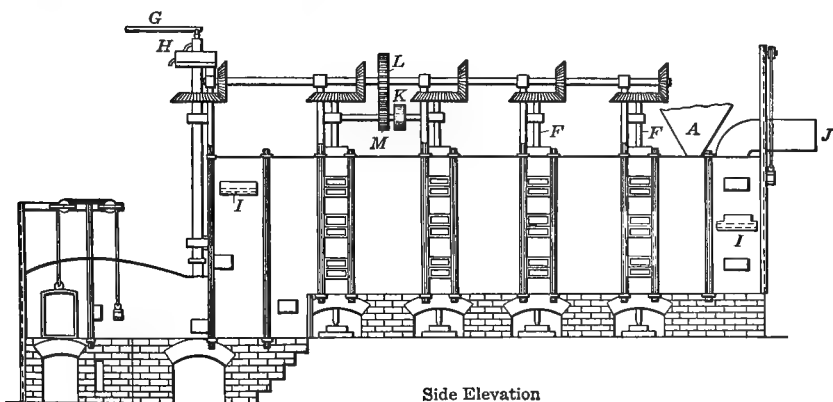
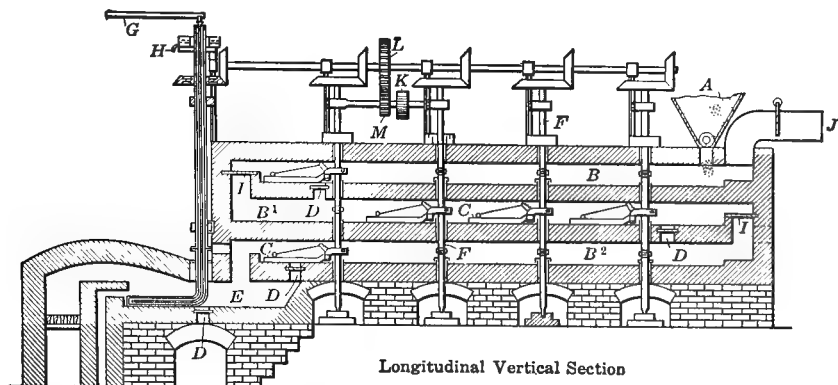
<sup>1</sup> *Loc. Cit.*

<sup>2</sup> Draper, F. W., Private Communication, November, 1910.

<sup>3</sup> Hutchinson, *Min. Sc. Press*, 1913, CVI, 171, 204.

freely at the tenth; the loss in weight is 17 per cent. A screen analysis of the roasted ore gave >100-mesh—12.5 per cent., >150—15.5, >200—25.5, <200—46.0 per cent.; a chemical analysis showed:  $\text{SiO}_2$  54.60,  $\text{Fe}_2\text{O}_3$  32.20, S (sulphide) 0.15, S (sulphate) 0.75,  $\text{Al}_2\text{O}_3$  3.00,  $\text{CaO}$  0.20,  $\text{MgO}$  0.13,  $\text{Cu}$  0.60, Se and Te 0.19, Sb 0.07 per cent. The furnace consumes per ton concentrate, 9 gal. California crude oil, and makes 1.5 per cent. flue-dust.

**73. The Merton Furnace<sup>1</sup>** shown in front elevation and vertical longitudinal section in Figs. 125–126, is similar to the simplex stationary Edwards fur



FIGS. 125–126.—Merton furnace.

nace as regards the general mechanical features. The leading differences are: that it has three super-imposed level hearths,  $B_1$ – $B_3$ , communicating by separate gas-passages,  $I$ , and drop-holes,  $D$ ; that there is a separate finishing-hearth,  $E$ ; that the spindles,  $F$ , 4 ft. 3 in. apart from center to center and making from 1.5 to 3 r.p.m., pass through the three hearths and are supported underneath the lowest hearth by foot-steps; that there are four rabble-arms to a hearth clamped to the

<sup>1</sup> Power, *Eng. Min. J.*, 1903, LXXVI, 775.

Simpson, *Tr. Inst. Min. Met.*, 1903–04, XIII, 30.

Merton, *Met. Chem. Eng.*, 1912, X, 432 (new design). U. S. Patent No. 1022961, April 9, 1912,

spindles; and that the spindle and rabble-arm of the finishing-hearth are water-cooled.

The furnace is 32 ft. 9 in. long over all. A roasting-hearth is 23 ft. 9 in. long, 8 ft. wide, 1 ft.  $4\frac{1}{2}$  in. high at the center and 9 in. at the sides; it has four doors on either side situated opposite the spindles; the finishing side has only one door. The furnace requires 2 h.p. The following capacities for 24 hr. are claimed: Kalgoorlie sulpho-tellurides 18-25 tons, blende-galena (with Zn 33, Pb 19, S 20 per cent.) reducing the S-content to 1.5 per cent., 8-10 tons; pyrite, 6-15 tons, depending upon the degree of desulphurization; sulphide copper ore up to 10 tons; arsenopyrite, 5-8 tons; and galena 8-20 tons.

**74. The Ropp Furnace.**<sup>1</sup>—The furnace represented in Figs. 127-131, is a single-hearth, straight-line mechanical furnace, usually 150 by 14 ft., with four exterior fire-places, *b*. 'Along the center of the hearth, *a*, runs a channel, *c*, 1.5 in. wide, through which extend vertically at equal distances heavy trapezoidal steel-plate arms, *d*, attached to four-wheel trucks, *e*, each carrying a rake of the width of the hearth with teeth set at an angle of 45 deg.

TABLE 25.—THE ROPP STRAIGHT-LINE FURNACE

Length of hearth, feet.....	105	100	150
Width of hearth, feet.....	11	14	14
Hearth area (deducting slot), sq. ft.....	1,120	1,367	2,050
Number of fireplaces.....	3	3	4
Length of single grate, feet.....	$4\frac{1}{2}$	5	5
Width of single grate, feet.....	4	4	4
Grate area, sq. ft.....	18	20	20
Ratio hearth to grate area.....	64 : 1	70 : 1	105 : 1
Number of carriages.....	4	4 to 6	6
Number of blades on carriage.....	26	32	32
Carriage makes circuit in (minutes).....	$3\frac{1}{2}$	$3\frac{1}{2}$	$5\frac{3}{8}$
Ore stirred every (seconds).....	52	53	53
Horse-power required.....	4 to 5	5	6 to 8
Depth of charge near fluebridge { Pyrite, inches... Matte, inches... Time ore remains in furnace (hours).....	$1\frac{1}{2}$ $1\frac{1}{2}$ 6 to 8	$1\frac{1}{2}$ $1\frac{1}{2}$ 6 to 8	$1\frac{1}{2}$ $1\frac{1}{2}$ 6 to 8
Tons in 24 hours { Pyrite..... Matte..... Dry gold ore.....	26 to 42 26 to 34 80 to 98	35 to 40 32 to 45 80 to 98	45 to 70 45 to 60 80 to 98
Per cent. sulphur in pulverulent roasted product, <sup>2</sup> { Pyrite... Matte... Dry gold ore	0.1 to 8 1 to 8 0.14 to 0.16	0.1 to 8 1 to 8 0.14 to 0.16	0.1 to 8 1 to 8 0.14 to 0.16
Number of men in 12-hour shift.....	$\frac{1}{2}$ to $\frac{1}{3}$	$\frac{1}{2}$ to $\frac{1}{3}$	$\frac{1}{2}$ to $\frac{1}{3}$
Tons of coal per ton of ore.....	$\frac{1}{8}$ to $\frac{1}{12}$	$\frac{1}{10}$ to $\frac{1}{14}$	$\frac{1}{12}$ to $\frac{1}{18}$
Gallons lubricating oil per ton of ore.....	15	14	13

<sup>1</sup> Built by Harron, Rickard and McCone, San Francisco, Cal.

<sup>2</sup> Character, composition and size of ore:

Pyrite: SiO<sub>2</sub> 18-30, Fe 20-30, Cu 0-6, Pb 0-20, S 20-30, Zn 0-10, per cent.; 30-mesh to  $\frac{1}{4}$  in.

Matte: Fe 20-40, Cu 0-50, Pb 0-18, S 18-30, Zn 0-4, per cent.; 20-mesh to  $\frac{1}{2}$  in.

Dry gold ore: S 1-2 per cent., 30-mesh and finer.

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There are six rakes working in pairs. They enter the hearth at *h*, where ore is introduced by the mechanical feeder, *i*, carry it slowly to the discharge, *j*, where it falls into trucks, *k*. The steel traction rope, which does not become hotter than the hand can bear, lasts about 1.5 years, and the rakes are thoroughly cooled on their return trips. The furnace has working doors on the sides, which permit access to the hearth and admit air.

The heat is regulated from the different fire-places; these have perforated fire-bridges to insure complete combustion with air preheated in the side-walls. The products of combustion pass off through the smoke flue, *w*. The furnace is built in two sections to allow for expansion and contraction; the sections are joined by bars of channel iron, which overlap and glide one within the other; they are tied independently, and the length of a longitudinal tie-rod does not exceed 50 ft. Table 25 gives some working details.

**75. The Wethey Straight-line Single-hearth Furnace.**—This is shown in plan, side- and end-elevations in Figs. 132–134. It covers a floor-space of 115 ft.  $3\frac{1}{2}$  in. by 16 ft. 5 in.; has a roasting-hearth 100 by 10 ft.; is fired from two pairs of exterior fire-places, *AA'*, the two forming a pair being placed opposite one another; the first pair, *A*, is 10 ft. 8 in. away from the feed-end; the second, *A'*, 22 ft. 8 in. distant from the first. The flame travels with the ore, enters a down-take, *B*, returns underneath the hearth, and passes near the feed into an underground flue, *C*, ending in a dust chamber connected with the stack. The moving and raking of the ore is accomplished by six rabble-arms, *D*, each with 20 exchangeable teeth, *E*. The arms, which form part of the carriages, travel on one set of outside rails, *F*, while the ore is being rabbled, and return on another, *G*, placed above the furnace. The continuous slot on either side is closed by tripping doors, *H*, through which enters most of the air necessary for oxidation. The carriages are connected and set in motion by two endless steel-link chains, *I*, passing over sprocket-wheels, *J*, at the ends of the furnace. The chains are kept taut by 2000-lb. weights attached to gliding journal-boxes of the upper sprocket-wheels; and the latter are prevented from sliding back by ratchet and pawl, *L*. The shaft, *M*, of the lower sprocket-wheel opposite the feed-end is connected by gearing, *N*, with the power furnished through belt and pulley, *O*.

The concentrate arriving in a mine car is emptied into two feed-hoppers, *P*, whence it passes through a curved chute-like feeder, *Q*, driven from a sprocket-wheel, into the path of the descending teeth of a rabble-arm to be carried into the furnace. This has two balanced inlet-doors, *R*; at the opposite end are similar outlet-doors, *S*. The roasted ore is discharged into suitable ore-cars, *T*. The roof of the furnace is supported by *I*-beam skewbacks, *U*, which are suspended by steel straps, *V*, from cross-beams, *W*, and braced by struts, *Y*, firmly connected with the vertical *I*-beams, *Z*; the latter are tied by rods, *a*, and spaced by distance pieces, *b*, which in their turn are let into the lower furnace-wall. The iron frame carries the supports, *c*, of the upper and lower tracks for the rabble-carriages. The furnace with its 1000 sq. ft. hearth area puts through in 24 hr. 70 tons sulphide copper ore, ranging in size from  $\frac{1}{2}$ -in. to 100-mesh, and having the following composition,  $\text{SiO}_2$  38, Fe 31, Cu 7.7, Zn 6.0, S 6.8; or 140 lb. per

square foot hearth area; the depth of the ore-bed near the feed is about 4 in. A rake makes the circuit in 13.5 min. The ore, remaining in the furnace about 4 hr., is stirred every 2 min.; the roasted ore retains 6.8 per cent. S. The furnace requires 15 h.p., and consumes 7000 lb. coal in 24 hr.; one man attends two furnaces in an 8-hr. shift. The cost of roasting in Butte was 34 cents per ton of ore.

H. F. Brown<sup>1</sup> has constructed a similar furnace.

**76. The Allen-O'Hara Furnace.**<sup>2</sup>—O'Hara<sup>3</sup> was the first to construct a straight-line mechanical roasting furnace with two superimposed hearths. The difficulties encountered at first by wear of chains, rabblers, and hearth have been overcome by Allen and by Brown.

The Allen-O'Hara furnace, shown in Figs. 135-138, has two hearths, *B* and *D*, 90 by 9 ft., and 5 pair of exterior fire-places, *Q*, two on the upper and three on the lower hearth, three being in use at one time. The grates are 5 ft. by 2 ft. 4 in. Each hearth has a pair of rails, *L'*, 3 ft. 5 in. apart, to carry six trucks, *K*, supporting the rabble-arms, each with 14 teeth of steel plate, to which are riveted white-iron shoes. Extra rabblers prevent the accumulation of ore on the rails. The trucks are connected by a weldless-link chain driven by sprocket-wheel, *F*, through shaft *G*, and kept taut by weight *J*, acting upon the gliding box *T*, of sheave *H*. Carriages, *M*, placed midway between the rabble-arms, prevent the sagging of the chain and permit exchanging it in parts when damaged. The backs of the carriages carry swinging double-bladed scrapers which prevent the ore forming a ridge along the center-line of the hearth not covered by the teeth of the rabble-arms.

The sprocket-wheel, *H*, is placed at a distance of 23 ft. from the end of the furnace to allow the chain and rabblers to cool. Beneath wheel *F*, is a grating, *P*, for repairing of chain and arms. The ends of the furnace are closed by horizontal turnstile doors, *N*, which are moved by the carriages. The ore fed mechanically at *A*, is moved over the upper hearth, drops through port *C*, at the opposite end on to the lower hearth where it travels in the opposite direction and is discharged into the brick hopper, *E*. The air necessary for oxidation enters through dampers in the side-doors, *R'*. At Butte, Mont., from 45 to 50 tons concentrate, ranging in size from  $1\frac{3}{4}$  in. to slime and averaging  $\text{SiO}_2$  23, Cu 14.6, Fe 23, Zn 2, S 37.4 per cent. were roasted in 24 hr., or 60 lb. per square foot hearth area. The ore lies about 3 in. deep near the feed, is stirred every 37 sec., with the carriages making the circuit in 3.75 min. It remains about 6 hr. in the furnace, and is discharged with a S-content of 8 per cent.; 100 lb. moist concentrate give 72.7 lb. roasted ore and 1 lb. flue-dust. A partial

<sup>1</sup> Hofman, *Min. Ind.*, 1897, VI, 450.

Strauss, *Min. Mag.*, 1911, V, 61, Casapalca smelter, Peru.

<sup>2</sup> Hofman, *Min. Ind.*, 1893, II, 432.

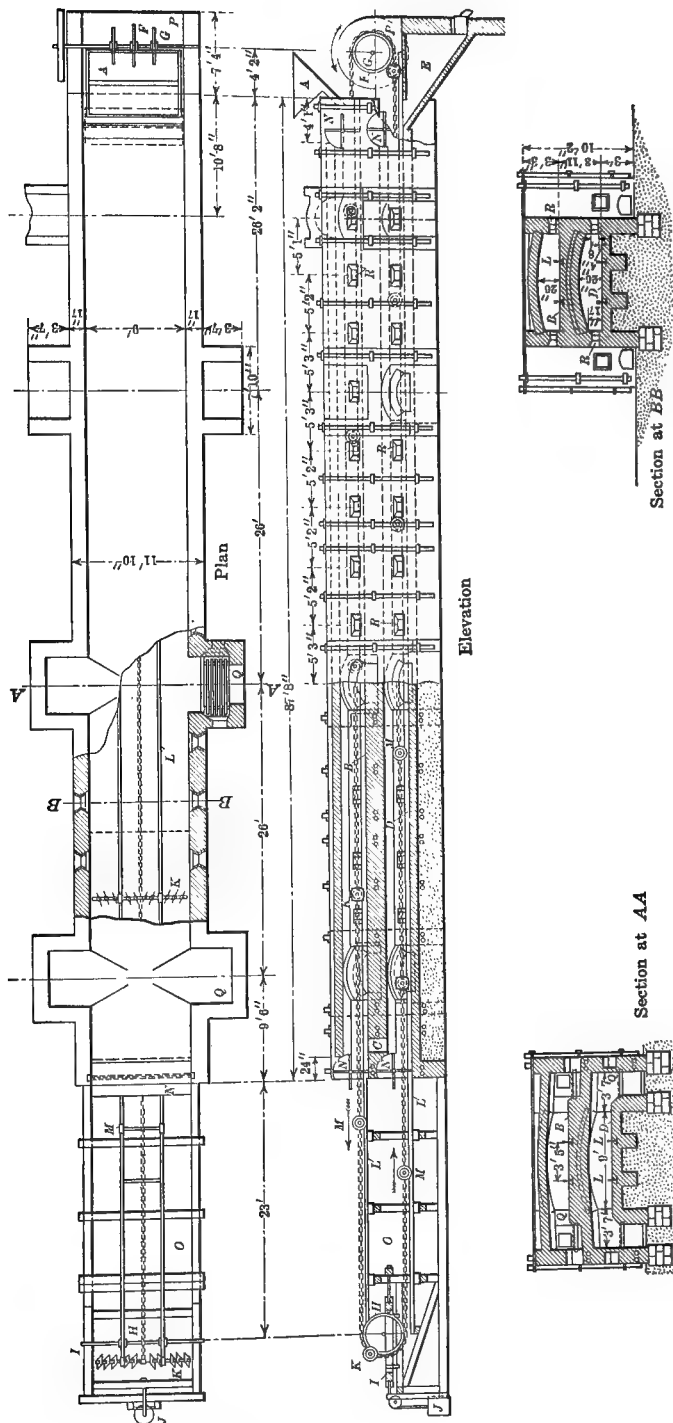
Wythe, *Eng. Min. J.*, 1893, LV, 460.

Kroupa, *Oest. Jahrb.*, 1894, XLII, 328.

Peters, *Min. Ind.*, 1894, III, 203.

Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 272.

<sup>3</sup> Küstel, G., "Roasting Gold and Silver Ores," A. J. Leary, San Francisco, Cal., 1880, p. 84.



FIGS. 135-138.—Allen-O'Hara two-hearth mechanical reverberatory roasting furnace.

Section at AA

Section at BB

analysis of an average sample of roasted ore gave, Cu 10.8, SiO<sub>2</sub> 31.6, Fe 38.0, S 7.6 per cent., and one of flue-dust, Cu 10.8, SiO<sub>2</sub> 34.4, Fe 36.5, S 8.2 per cent.

The furnace requires 3.64 h.p.; 100 lb. coal are consumed per ton of ore; the labor needed in an 8-hr. shift is  $\frac{1}{2}$  car-man who brings the raw ore,  $\frac{1}{2}$  fire-man, 1 wheeler who removes the roasted ore, and  $\frac{1}{8}$  repair-man during the day-shift only. The rabble-arms last about 1 year, the teeth 6 weeks, the flange-wheels 6 months, the chain 1 year. The cost of roasting at Butte in 1904 was \$0.78 per ton.

The Brown-O'Hara furnace is referred to below.

**77. Wethey and Keller Multiple-hearth Furnaces.**—The WETHEY MULTIPLE HEARTH STRAIGHT-LINE FURNACE, shown in vertical cross-section in Fig. 139, is a double furnace with four superimposed hearths, 50 by 5 ft., which have slots alternately at opposite ends in order that the ore fed near one end of the top hearth, when moved to the other by mechanically driven rakes, may drop on the second hearth and so on until it reaches the discharge on the bottom hearth. The furnace is built in an iron framework as is the single-hearth furnace given in Figs. 132-134. The framework consists of vertical channel-beams, *a*, joined by riveted horizontal castings (not shown) which form the supports for horizontal I-beams, *b*, carrying the three upper hearths. Channel-beams *a*, are braced by tie-rods *c*. The brick bottoms of the upper hearths are laid on steel plates, *d*, which rest on 3-in. I-beams, *e*. Along the inner sides of each hearth run longitudinally two 6-in. I-beams, *f* and *g*; the lower ones, *f*, rest on channel-beams, *b*, and carry the tracks as well as the angle-irons against which are built the inner side-walls; the upper beams, *g*, are suspended from channel-beams, *b*, by castings, *h*, and form the inner skewback of the roof; the outer skewback, *i*, is backed by vertical channel-beams, *a*. The three upper hearths are supported independently of one another.

The ore is raked and moved by rabble-arms *j*, which are attached to two endless link-belt chains passing over two pairs of sprocket-wheels (not shown). The 2-in. slots in which the rabble-arms travel are closed by tripping doors. The fire-boxes are placed on the levels of the second and fourth hearths, on which the fire-gases enter the furnaces to travel in a direction opposite to that of the ore. The double furnace with eight hearths, 50 by 5 ft., has 2000 sq. ft. hearth area; there are four fire-places with grates 38 by 33 in., which gives a grate area of about 80 sq. ft., or a ratio of hearth to grate area of 25 : 1. There are eight rabble-arms to a furnace, each with 14 teeth; four arms make the circuit of two floors in 185 sec., hence the ore is stirred once in 46 sec.

The concentrate treated at Butte ranged in size from 12- to 4-mesh, and assayed SiO<sub>2</sub> 10, Fe 35, Cu 10, Zn 5, S 40 per cent. The depth of charge near the feed is about 4 in.; the ore remained in the furnace from 8 to 10 hr., and was discharged with about 8 per cent. S. The furnace put through in 24 hr. 45 tons concentrate, consumed 110 lb. slack coal and 0.1 gal. black lubricating oil per ton of ore, required 1 man per shift, and made 0.5 per cent. flue-dust.

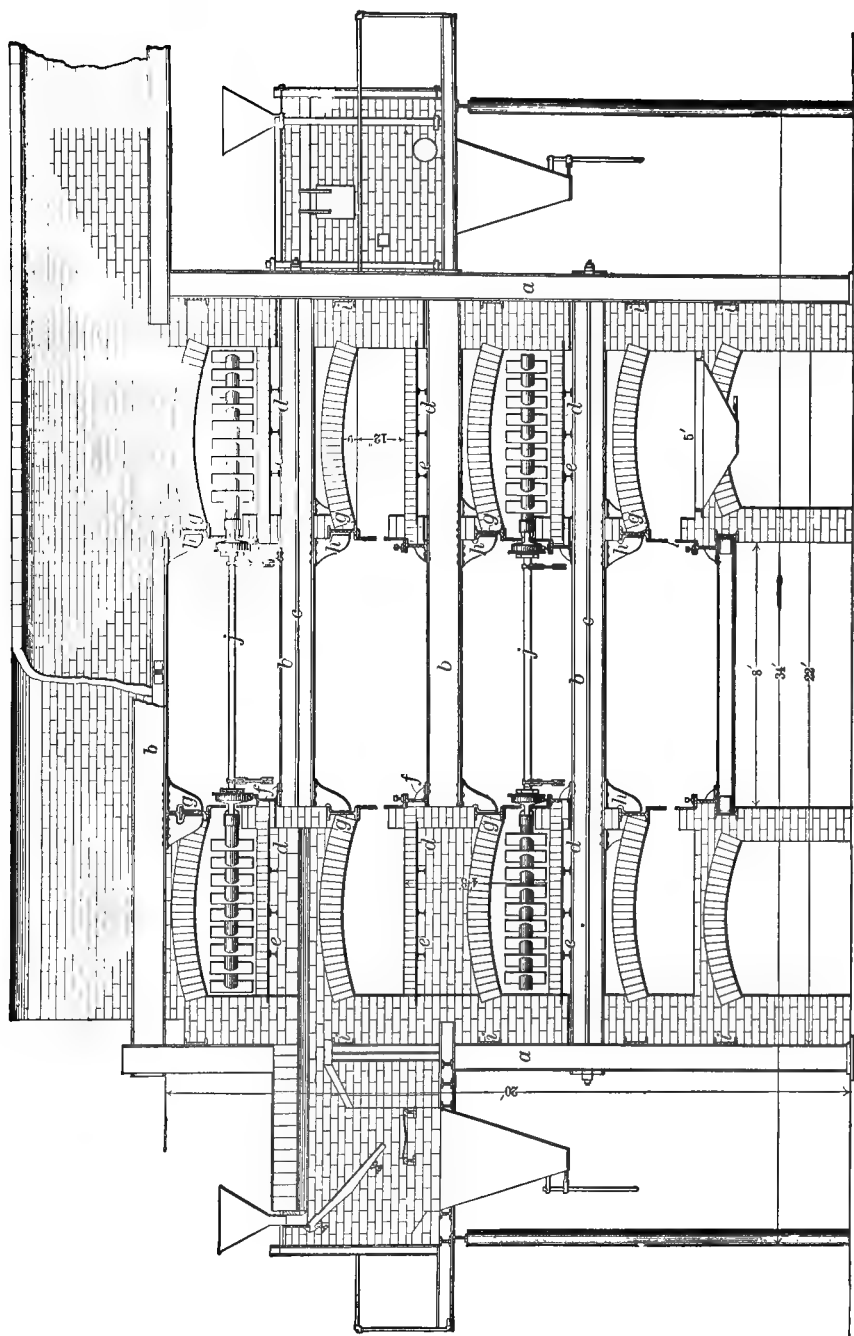


FIG. 139.—Wethey multiple-hearth mechanical reverberatory roasting furnace.



through flues *b* and *c* and an underground passage *d* to the stack. They thus envelop the roasting part of the furnace by hot gases and thereby diminish the loss of heat by radiation. The rabbling apparatus, which required from 2 to 3 h.p., is complicated and probably has become obsolete as have most rabbling-devices which move to and fro over a hearth.

The furnace treated in 24 hr. 45 tons of Butte concentrate, reducing the S-content from 40 to 7 per cent., consumed 1.25 tons of slack coal, and required  $\frac{3}{4}$  man per shift. At Salt Lake City it roasted in 24 hr. 35 tons of wet pyritic concentrate containing some Cu, 8 per cent. Pb and 30 per cent. S, reduced the S-content to about 3 per cent.; and consumed 2 tons of slack coal.

**78. The Brown Horseshoe Furnace.**<sup>1</sup>—The late H. F. Brown constructed three types of roasting furnaces, all of which have two patented improvements, Fig. 142, a recessed chamber on either side of the hearth for the reception of the mechanism of the rabble-carriages, and a continuous slot for the passage of the rabble-arms from the chambers to the hearth. His three types of furnaces are the Horseshoe, discussed below; the Elliptical,<sup>2</sup> in operation at one time at the Golden Reward works, Deadwood, S. D., for roasting silver-gold ores; and the Straight-line,<sup>3</sup> which is similar to the Wethey furnace shown in Figs. 132–134.

In the HORSESHOE FURNACE, represented by Figs. 141–148, the roasting hearth, Fig. 141, occupies five-sixths of the annular space, the remaining one-sixth forms an open span, *l*, for the feed and discharge of ore, and for the cooling of the rabbles. The hearth, *m*, 135 by 8 ft., has a roasting surface of 1080 sq. ft. which is heated from three exterior fire-places with grates 3 by 5 ft., giving a ratio of hearth to grate area of 24 : 1. The first fire-box is placed about 60 ft. from the feed-end of the furnace; the other two are 35 and 40 ft. apart.

The flame from a fire-box enters the furnace through the roof, *q*, Fig. 143; it spreads uniformly under the latter and does not strike the ore. Ore and flame travel in opposite directions. The stack, *i*, carries off the gases. In the center of the furnace, Fig. 141, is an engine, *a*, varying from 5 to 8 h.p. (only two are required) which drives the mechanical feeder, *b*, and the endless cable, *c*, running over sheaves, *d*. Opposite each sheave is a door, *e*, which gives access for oiling and repairing, and admits air for cooling the bearings and for roasting the ore. The doors, *f*, on the outer side of the furnace are far enough apart to furnish access to the hearth when the outer wall, *g*, between the doors and the tiling, *h*, has been taken out.

The rabble-carriage, Figs. 147–148, consists of an L-shaped frame with one flat-tread wheel, *x*, running in the outer, and two double-flanged wheels, *y*, in the inner passages, Figs. 142, 143. The front inner wheel, Fig. 148, has the cable-grip, *z*. The tooth or point, *t*, Fig. 147, is plow-shaped, of cast iron, and is keyed to the cast-steel rabble-arm, *u*, Fig. 146, which is attached to the stirrer-arm, *v*, reaching across the hearth. Arms, *u*, are lowered as the plows wear off;

<sup>1</sup> Allis-Chalmers Co., Milwaukee, Wis.

<sup>2</sup> Brown, *Eng. Min. J.*, 1896, LXII, 80.

Rothwell, *Min. Ind.*, 1896, v, 270.

<sup>3</sup> Hofman, *Min. Ind.*, 1897, VI, 459.

when a crust forms on the working hearth, they are lowered one at a time to cut underneath. The arms are placed about 12 in. apart and are mismatched so as to cover the whole surface of the ore. One carriage, Fig. 147, has side-stirrers, *w*, to prevent the accumulation of ore. There are two carriages to a furnace which are alternately attached to and released from the continuously traveling cable, *c*. The ore is delivered at *b*, Fig. 141, by an automatic feed, which discharges with every passage of a car a weighed amount of ore on to the hearth outside of the swinging door, *j*. The ore then enters the furnace, travels over the hearth in from 12 to 14 hr., leaves it by the other door, *k*, and is discharged into wheelbarrows or trucks placed at *l*. A heavy sulphide ore ignites at a distance of about 15 ft. from the flue-end or in about 1 hr. after it has been fed; an ore running low in S will be brought to the kindling temperature in from 2 to 2½ hr.

One traveling stirring-carriage (not shown), after leaving the furnace at *k*, strikes the other carriage, *m*, at rest in the open space, *b*, and pushes it along until its grip-lever comes in contact with a fixed stop and is forced down, when it grips the cable which draws the carriage into the furnace. At the same time the heated carriage is automatically released, comes to a stop in the place just occupied by carriage, *m*, and cools in the open space for 1 to 3 min. In this manner the two carriages are used alternately at intervals of 1 to 3 min. and do not become sufficiently heated to be much affected by their passages through the furnace.

Fig. 142 gives some details of construction. The heavy cast-iron frames, *e* and *f*, of the inner and outer doors, carry 9-in. channel-beams, *n*, which are backed by buckstays, *o*, secured in their turn by tie-rods, *p*. Thus the roof is supported independently of the brickwork between the doors, which can be taken out to furnish access to the interior. The sheaves, *d*, are supported in the doors outside of the inner recess-chamber and thus remain cool. The tiling, *h*, is set in the floor and is easily removed when occasion calls for it. The tiling, *s*, forms part of the roof, and special care must be had to secure it firmly. The inner passage shows a T-rail for the inner double-flanged wheels of the stirring carriage; in the outer passage is a smooth rail for the outer flat-tread wheel giving room for expansion and contraction. From 1 to 2 per cent. flue-dust is ordinarily made.

The furnace, as seen by Table 26, has been used for roasting different kinds of ore. The advantages claimed for the recessed chambers as regards the protection of the stirring mechanism have been much exaggerated. The leading disadvantage<sup>1</sup> lies in the fact that the carriage in being moved over the hearth is pulled on the inner side only. The result is that the ore on the outer side is not as well stirred as that on the inner because the plows pass over obstructions that are forming on the working bottom instead of plowing through them; and, secondly, in consequence of this the carriage frequently jumps the track and creates havoc in the furnace.

<sup>1</sup> Testimony of W. H. Smyth in case *H. F. Brown vs. Metallic Extraction Co.* U. S. Circuit Court of Appeals, Eighth Circuit, pp. 453, 457, 459, 461.



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TABLE 26.—WORK OF THE BROWN HORSESHOE FURNACE

Character of ore	Raw ores				Ore roasted in 24 hours, tons	Fuel		Ratio hearth to grate area	Ore roasted per sq. ft. hearth area, pounds	Roasted ore, sulphur, per cent.
	Size, mesh	Sulphur, per cent.	Zinc, per cent.	Lead, per cent.		Wood, cords	Coal, tons			
Pyrite-chalcopryite.....	4	40-45	3-5	None	35	3½	.....	24 : 1	48.8	4.5
Galena-blende.....	4	20-25	8	15	25	.....	4 <sup>1</sup>	23.3 : 1	47.6	3.5-4
Copper matte.....	40	20	40 Cu	15	20	.....	3.25	35 : 1	38.0	6.0 <sup>2</sup>
Siliceous ore with pyrite..	30	2.5	1.5 As	.....	95	6	.....	32 : 1	131.0	0.3
Siliceous ore with pyrite..	16	2-5	.....	.....	50	.....	4.5 <sup>1</sup>	28.66 : 1	77.0	0.5
Siliceous ore with pyrite..	20	2-3	2.5 As	.....	65	6	.....	32 : 1	90.0	0.5
Siliceous slimes.....	60-400	2-5	.....	.....	65	.....	5.25	31.1 : 1	92.8	0.3
Blende.....	12	28	56	1.5	12	.....	8.00 <sup>3</sup>	22.8 : 1	22.0	0.8

<sup>1</sup> Lignite. <sup>2</sup> Present as sulphate, the aim of the roast being to peroxidize the iron and convert as much copper as possible into soluble sulphate. <sup>3</sup> Refuse slack coal.

**79. The Pearce Turret Furnace.**<sup>1</sup>—This is the second circular or turret-shaped mechanical reverberatory roasting furnace, with a space left open for the feed and discharge of ore, which has been used to a considerable extent in the roasting of sulphide copper ore. It is built with one, two, and six hearths.

THE SINGLE-HEARTH FURNACE is represented in plane and vertical section in Figs. 149–150. These show a circular hearth, 6 ft.  $\frac{1}{2}$  in. wide (area 505 sq. ft.),<sup>2</sup> heated from three exterior fire-places, *b*, the fire-gases traveling in a direction opposite to that of the ore, and passing off through the down-take, *c*. The outer wall has a number of doors, Fig. 152, usually closed, which furnish access to the hearth; between each pair of doors and 2.5 in. above the level of the hearth, Figs. 149 and 152, is a horizontal flue, *e*, 8 in. wide, through which air, warmed in its passage, can be admitted at the surface of the roasting ore, provided the draft in the furnace is sufficiently strong. The inner wall is divided by the rabble-arm slot, *f*, into two parts. The lower one, *a'*, is erected in the usual way; the upper one is suspended by stirrups, *g*, in angle-irons, *V*, from radial I-beams, *h*, and cross-beams, *i*, and is braced by radial struts, *c''*. The I-beams are supported by the outer wall and the central column, *j*, and the cross-beams by the I-beams. The stirring mechanism turns over and moves the ore, fed automatically through the roof, and discharges it on the side opposite the feed. It consists of a pair of horizontal pipe-arms, *n*, which are placed diagonally in a hollow hub, *o*, revolving around the stationary hollow central cast-iron column, *j*, and are supported at *r* by rollers traveling on track *z*. A rabble-arm is made up of two pieces of 5-in. gas-pipe joined at *r*; the outer part reaching into the furnace is provided with the necessary rabble-blades, *m*. The blades, of  $\frac{1}{4}$ -in. steel, are graduated in length and direction from the inner to the outer circle of the hearth so that the ore on the outer circle, which has to travel the greater distance, shall remain in line with that of the inner circle. The continuous slot, *f*, in the inner wall is closed by a 12-in. band of sheet-steel, which is carried by the two rabble-arms and two reserve-arms, and is pressed against the slot by weighted bell-cranks, *u*, attached to a circular angle-iron, *z*, also carried by the arms. The four arms are braced by rods, *q*. The cast-iron column, *j*, is connected through pipe, *b'*, with a blower. The air passing through *b'* and *j*, enters hub, *o*, acting as an air-box, and thence into the rabble-arms keeping these cool, and is slightly warmed and delivered (between the blades) into the furnace through small pipes which point downward, and through horizontal holes in the arms situated between blades and pipes.

The rabble-arms receive their motion through spur-wheels, *s*, centered by rollers, *t*, which are in gear with pinions, *c'*, on pinion-shafts, *v*; the latter are driven by bevel-gearing, *w*, and main shaft, *x*. The arms travel at an average speed of 75 ft. per min., taking the circumference of the center of the hearth as the line of measurement. This makes 53 sec. the time of a complete circuit with a 6-ft. hearth, and causes the ore to be rabbled once in 26.5 sec.

<sup>1</sup> Stearns-Roger Mfg. Co., Denver, Colo.

<sup>2</sup> Furnaces with hearths 7 ft. wide (area 609 sq. ft.) and 8 ft. wide (area 788 sq. ft.) have been built.

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The lower I-beams, *y*, Fig. 151, serve as inner braces of the furnaces; they hold the boxes of the vertical pinion shafts, and carry the circular track, *z*, which bears the weight of the rabble-arms.

The ore is fed mechanically from the hopper, *d'*, by a device which is controlled through shaft, *e'*, connected by pulleys, *f'* and *f''*, and belting, *g'*, with the main driving shaft, *x*. Thus the rate of feed is regulated by the speed of the rabble-arms. A rabble-arm, after leaving the discharge-opening, travels over the open space and arrives at the uncovered part of the hearth which receives the ore from the feeder. It spreads out this ore and enters the covered hearth by the swing-door, *i'*, Fig. 152. As at first the ore is only dried and brought to the kindling temperature, any air admitted at this period would retard the process. It is therefore automatically controlled by a butterfly-valve, *j*, in the arm, which closes as it strikes the first stop, *k'*, and opens again when it reaches the second stop, *m'*. The arm leaves the covered hearth by the second swing-door, *i''*, Fig. 152, carrying with it some roasted ore which drops through the discharge-hopper *n'* into a truck, the fumes being carried off by the sheet-iron stack *o'*. The ore remains on the hearth about 6 hr.

The rabble-teeth last from 4 to 6 weeks with pyritic ore assaying about 40 per cent. S; the outer part of a rabble-arm which is exposed to heat and fumes about 12 months. The furnace requires 2 h.p. Temperature-measurements have been published by Clevenger.<sup>1</sup> The cost of roasting in Butte is about \$1.00 per ton. Some work done by this furnace is given in Table 27.

THE TWO-HEARTH FURNACE.—The "double-deck" furnace, with its two superimposed hearths separated by an air-space of 2 ft., has a height of 16 ft. 6 in. against 11 ft. of the single-deck, and twice the hearth area. Each hearth has the two usual rabble-arms. A horizontal section through the upper hearth is shown in Fig. 152 and a vertical section through the entire furnace in Fig. 151. The details are nearly the same as those of the single-hearth furnace; hence the different parts common to Figs. 149, 150, 151, 152, are designated with the same letters.

The lower part of the inner wall of the upper hearth rests on I-beams, *h*, while the upper parts of both hearths are suspended and held in place as with the single-hearth furnace. Underneath the lower hearth is a dust chamber through which passes the driving-shaft of the lower rabble-arms; it is enclosed by a 5-in. pipe for protection against sulphurous gases. The upper driving-shaft, directly connected with the main pulley, transmits the power to the lower shaft by means of bevel-gearing and a vertical shaft. The furnace requires 5 h.p. It has two upper and two lower fire-places.

Fig. 151 shows a step-grate, *k*, which is used with non-caking coal or lignite; there is also a curtain arch, *m''*, over which the flame travels for a short distance, and is thus prevented from overheating the roasting ore.

The ore is fed on to the upper hearth as in the single-hearth furnace; it travels in the direction of the arrow over the upper hearth, drops through slot,

<sup>1</sup> *Met. Chem. Eng.*, 1913, XI, 449.

TABLE 27.—WORK OF THE PEARCE SINGLE-HEARTH TURET FURNACE

Hearth	Roasting material		Produc- tion in 24 hr., tons	Sulphur <sup>1</sup> in roasted material, per cent.	Material roasted per sq. ft. of hearth area, pounds	Hearth to grate area, ratio	Coal consumed per ton of ore, pounds	Ore remains in fur- nace, hours	Rabble- arm makes one cir- cuit in seconds	Authority
	Kind	Size, mesh								
7 <sup>1</sup>	609	Pyrite.....	SiO <sub>2</sub> 25-30, S 35.....	22	3	72	15 : 1	318	.....	Pearce.
7 <sup>1</sup>	609	Matte.....	Cu 40-50, Pb up to 15.....	12	3	40	15 : 1	583	.....	Pearce.
6	505	Pyrite.....	S 43.....	16	6-7	63	.....	328	6	Peters.
6	505	Matte.....	Cu 15, Pb 11, S 17.....	11	3-3	40	.....	.....	6	Peters.
6	508	Pyrite.....	SiO <sub>2</sub> 10, S 45.....	9	None	35	.....	.....	6	Peters.
6	505	Mixed sul- phide.....	SiO <sub>2</sub> 18, Fe 20, Zn 15, Cu 11, S 31.....	15	6-7	60	.....	.....	6	Peters.
6	505	Mixed sul- phide.....	SiO <sub>2</sub> 18-30, Fe 20-30, Pb 0-20, Zn 0-8, CuO, S 25-30.....	14-16	1-8	60	.....	333	4-5	Private notes.
6	505	Matte.....	Fe 20-40, Pb 0-18, Zn 0-15, Cu 0-50, S 18-20.....	10-14	1-7	47	.....	333	4-5	Private notes.
6	505	Siliceous gold ore.....	S 1-3.....	50-60	0.2	210	2	2	.....	Stearns-Rogers Mfg. Co.
6	505	Matte.....	Fe 55, Pb 12, S 29.....	30	5-6	118	17 : 1	333	6	Setz.
6	505	Butte concen- trate.....	Cu 7, Fe 24, Zn 12, S 32, SiO <sub>2</sub> 23.....	14	7-8	56	15 : 1	400	6	Private notes.

<sup>1</sup> Three fire-places, each 4 ft. 6 in. by 3 ft. <sup>2</sup> Oil burners installed in crown of arch.

$p'$ , on to the lower hearth, and continues to move similarly on the lower to the discharge.

A double-deck furnace with hearths 6 ft.  $\frac{1}{2}$  in. wide, having a roasting area of 1010 sq. ft., treats in 24 hr. 30 tons concentrates (59 lb. per square foot hearth area) containing Cu 12, Zn 8, S 35, Fe 25, As 3, SiO<sub>2</sub> 16 per cent.; reduces the S-content to 6–7 per cent.; and burns 400 lb. slack coal per ton of ore. A furnace with two 7-ft. hearths (area 1218 sq. ft.) treats 42 tons (69 lb. per square foot hearth area) with a similar elimination of S, and consumes 182 lb. coal per ton of ore. Power and attendance are the same as with the 6-ft. hearth. The high zinc-content of the ore (Gagnon mine) accounts for the small roasting capacity. Comparing the 6- and 7-ft. furnaces, the quantity of ore roasted per square foot hearth area is increased by 15 per cent. in favor of the latter, and the fuel-consumption reduced by 55 per cent.

THE SIX-HEARTH FURNACE<sup>1</sup> was in operation at the works of the Colorado Smelting and Mining Co., Butte, Mont. It has six superimposed hearths, the roof of one forming the hearth of the next one above. The stirring mechanism and the passages of ore and gas are the same as in the R. Pearce double-deck furnace, there being six hearths instead of two. The ore fed at the top passes successively over the six hearths to be discharged from the last. The rabble-arms of the three lower hearths are driven by gearing from below, those of the three upper hearths from above. The main lower shaft forms the continuation of the pulley-shaft; the main upper shaft is connected with the lower by a vertical shaft and bevel gearing. There are two fire-places, one, 3 ft. by 3 ft. 2 in., for the top; the other, 4 ft. 3 in. by 3 ft. 2 in., for the bottom-hearth. The inner walls above the horizontal continuous slots of the rabble-arms have cantilever supports with trussed cords from the stationary central column. This makes a complicated structure, requiring a large number of iron parts of various sizes and weights. The iron parts of the furnace (32 ft. in diam., 20 ft. 9 in. high, hearths 7 ft. wide, distance from roof to roof 2 ft. 9 $\frac{1}{2}$  in.) weigh 165 tons. A hearth has the usual two rabble-arms. The furnace roasted in 24 hr. 56 tons of Butte concentrate, or 38 lb. per square foot hearth area; made 4 per cent. flue-dust; and consumed 28.5 lb. slack coal per ton of ore. The amount of ore roasted per square foot hearth area shows no improvement over the double-deck furnace, but the fuel consumption is greatly reduced, thus showing the benefit of diminishing the radiation loss of heat through doing away with the air-space between hearths in the double-deck furnace. In all probability another furnace of this type will not be built, on account of the expense, the complicated structure, and the inaccessibility of the machinery.

**80. The Brückner Furnace.**—In 1864 the late W. Brückner constructed his furnace in San Francisco. In 1867<sup>2</sup> he introduced it in Colorado for the roasting of pyritic concentrate and the chloridizing of silver ores. While it has changed in

<sup>1</sup> R. F. Pearce, U. S. Patent No. 670071, April 2, 1901.

Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 274.

<sup>2</sup> *Dingl. Polyt. J.*, 1868, CXC, 288; *Am. Min. J.*, 1869, VIII, 227; *Berg. Hüttenm. Z.*, 1869, XXVIII, 130.

the details of construction from the original and some later forms,<sup>1</sup> it retains the same general characteristics, viz., a brick-lined horizontal cylinder of boiler iron which revolves on friction rollers between a fire-box and a flue, and stirs the ore-charge automatically.

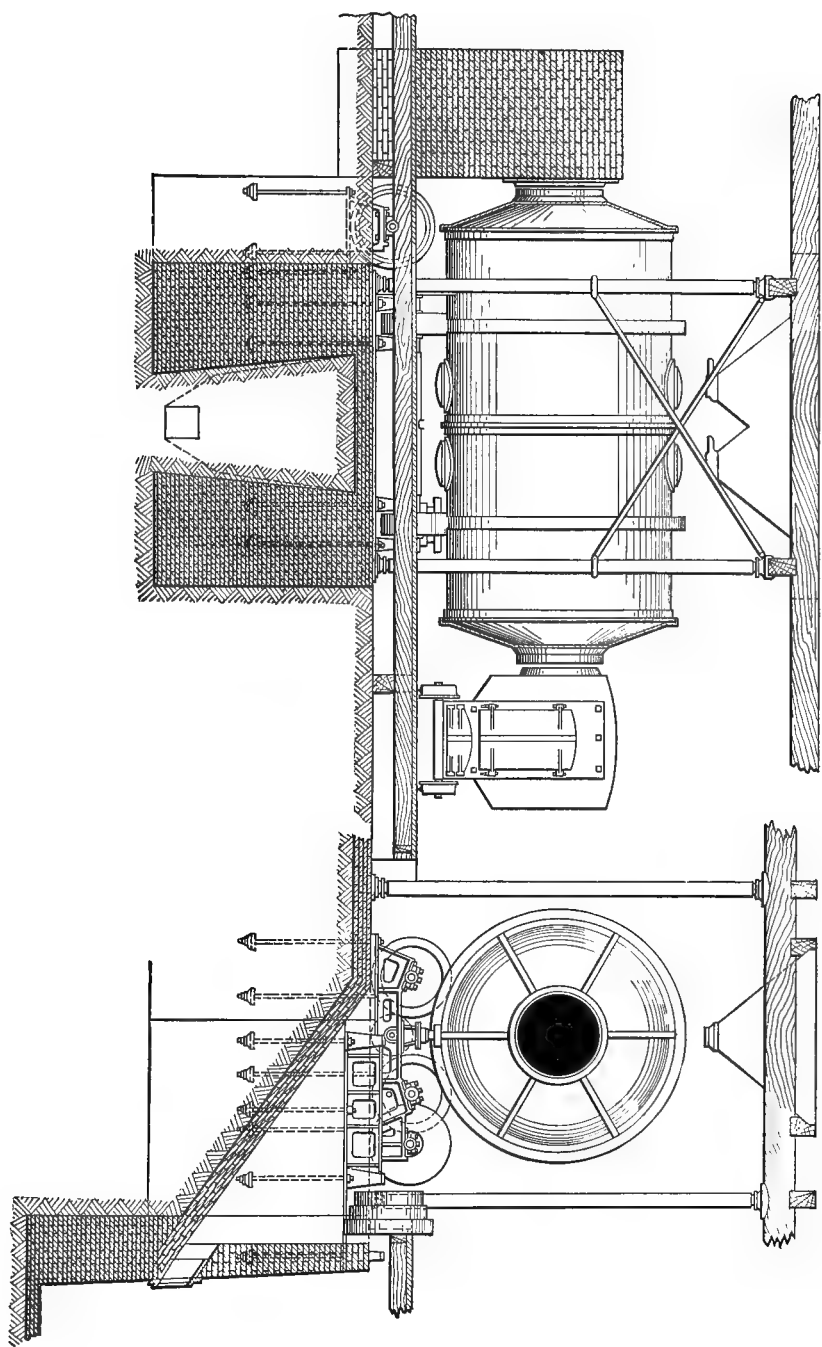
Figs. 153-154 represent a modern furnace with movable fire-box as built by the Allis-Chalmers Co., Milwaukee, Wis. The cylinder ending in truncated cones (heads) revolves with two friction-rings on two pairs of carrying-rollers. One of the carrying-roller shafts is rotated by a spur-wheel gear driven by a pinion shaft. The movable fire-box runs on tracks placed at right angles to the axis of the furnace so that one fire-box can serve several furnaces when these are roasting ores running high in S. The fire-box is lined with fire-brick; the furnace, 16 ft. long by 8 ft. in diameter, is lined with fire-brick in the heads and with hard-burnt red brick in the body. It has four discharge-openings, two of which serve for receiving the charge dropped from the feed-hoppers above. The furnace requires 2 h.p. making 8.5 r.p.h.; it rough-roasts a charge of 15 tons of Butte concentrate in 24 hr. Two hours' time is taken up with drying the ore, 4 with bringing it to the roasting temperature, and the remaining 18 with roasting, including charging and discharging. The number of revolutions made while discharging is greater than that while roasting. In 1895 the Anaconda (Mont.) works had 156 cylinders in operation. When the ore burns, the fire-box can be removed to a neighboring furnace. The duration of the roast without a fire-box is governed by the character of the ore and the altitude of the roasting plant. Thus a Colorado gold-ore concentrate, at Omaha, Neb., 800 ft. above sea-level, required 8 hr. heating, and then roasted 36 hr. without any additional firing. The same class of ore at Denver, Colo., 5000 ft. elevation, roasted without the fire-box only 12 hr.; and at Leadville, Colo., 10,000 ft. elevation, firing was required most of the time.

In roasting ores running low in S, the fire-box is stationary, or movable in the direction of the axis of the furnace. The main difficulty encountered here, when coal is used as fuel, is the admission of the air necessary for oxidation. It is overcome by introducing between the necks of the fire-box and the head of the cylinder a steam- or air-jet, which stirs up the heavy sea of SO<sub>2</sub> floating upon the ore and causes it to be carried off with the fire-gases. The late C. H. Aaron<sup>2</sup> made the neck of the fire-box muffle-shaped, kept that of cylinder-head circular, and thus left uncovered a segment which could be more or less closed by a swinging plate pivoted to the fire-box. In this way, cold air, heavier than hot SO<sub>2</sub>, entered the furnace, raised the SO<sub>2</sub> and came at the same time in contact with the charge.

The ore in the revolving cylinder forms a segment of a circle the cord of which is inclined upward in the direction of the motion of the cylinder. Whenever the angle of incline exceeds that of the angle of repose, the ore glides downward or turns over at the top; often both changes take place together and cause

<sup>1</sup> Locke, *Tr. A. I. M. E.*, 1873-74, II, 295.

<sup>2</sup> *Eng. Min. J.*, 1886 XLII, 184; *Eighth Ann. Report*, State Mineralogist of Cal., 1888, p. 849.



FIGS. 153-154.—Brückner furnace.

a satisfactory renewal of surface for oxidation.<sup>1</sup> However, these continued sudden motions of the ore stir up the fine particles which are carried away by the gas-current and form flue-dust which is rarely less than 5 per cent. of the weight of the ore, and usually a great deal more, reaching even 25 per cent. Further, on account of the shortness of the furnace, the fuel consumption is large, 400-500 lb. coal per ton of ore; there is danger of the ore balling together; the roasted ore is dark brown (more  $\text{Fe}_3\text{O}_4$  than  $\text{Fe}_2\text{O}_3$ ) and dense (from pellets), and the cost of working is high (\$1.25 per ton in Mont.).<sup>2</sup> These reasons, in addition to the small roasting capacity as compared with modern furnaces, have made the Brückner furnace almost obsolete for the rough-roasting of sulphide copper ore. It is still in operation for roasting mixed lead-copper ores, but here it will have to yield to blast-roasting. The only field that still remains open is the chloridizing roast of silver ore,<sup>3</sup> and here other furnaces have encroached upon the domain formerly held by Brückner.

**81. Roasting in Automatic and in Muffle-furnaces.**—Automatic furnaces such as the Stetefeld, Spirek, Hüttner, etc., which serve for roasting silver and quicksilver ores, have been little used, if at all, with copper ores. For muffle furnaces, which are expensive to build and operate, the same holds good although to a less degree, as sometimes concentrates of decrepitating chalcopyrite have been roasted in this manner. There may be mentioned the Douglas furnace,<sup>4</sup> an inclined revolving cast-iron cylinder with central flue for fire-gases and annular space with tile-partitions for the slow and continuous descent of the ore. The furnace was in operation at the works of the Kansas City Smelting and Refining Co. to furnish from a mixed sulphide concentrate the  $\text{SO}_2$  necessary for the Hunt-Douglas process (§ 223). The Jones rotary Kiln<sup>5</sup> in use at the Hinckley Fiber Company's works, Hinckley, N. Y., is similar.

**82. Blast-roasting in General.**—The blast-roasting of sulphide copper ores has not become so prominent as the blast-roasting of lead ore. This is due in part to the difficulties encountered in the operation, but mostly to the fact that a sulphide copper concentrate is easily roasted in a MacDougall furnace, and more cheaply than by any blast-roasting device, and smelted in a modern large-size reverberatory furnace, often at less cost than coarse material in a blast-furnace. Blast-roasting will therefore probably be restricted mainly to districts in which reverberatory smelting on a large scale is not practicable or profitable. This is the cause of scarcity of blast-roasting plants in the United States; they are more common in Spain, Australia, and other countries. Blast-roasting of sulphide copper ore and copper matte, in pots, has received in Australia<sup>6</sup> special names, such as Knapp-Kunze and McMurtrie-Rogers processes.

<sup>1</sup> Warwick, Progress of roast in large and small Brückner, *Min. Mag.*, 1905, XII, 196; plot by Austin, *Min. Ind.*, 1906, XV, 252.

<sup>2</sup> Weinberg, *Eng. Min. J.*, 1886, XLI, 166.

<sup>3</sup> Raymond, "Improved Two-cylinder Furnace," *Tr. A. I. M. E.*, 1885-86, XIV, 576.

<sup>4</sup> *Eng. Min. J.*, 1886, XLII, 114, 183.

<sup>5</sup> Wilson, A. W. G., "Pyrites in Canada," Canada Dep't of Mines, 1912. Kiln manufactured by The Pyrite Engineering Co., Carthage, N. Y.

<sup>6</sup> Radcliff, *Min. Sc.*, 1909, LX, 67.

The principles of blast-roasting have been discussed elsewhere.<sup>1</sup> Both up-draft and down-draft apparatus are in use at present, the latter are, however, replacing the former. With pyritic ores, the down-draft furnace has the disadvantage that the molecule of S which is distilled from pyrite is likely to clog the pipes and the fan.

The size of ore best suited is probably  $\frac{1}{4}$  in.; fluxes added may be coarser, but preferably not over  $\frac{1}{2}$  in. The coarser the charge-components, the less water will have to be added to the charge to keep it porous. Thus with a coarse charge the amount of water mixed in may be as low as 2 per cent., while with fine particles it may reach 12 per cent. The S-content must be high enough to furnish by its oxidation the heat necessary for carrying on the process; it may reach 20–25 per cent. as long as that of the charge need not be reduced to below 6–8 per cent. The leading fluxes are  $\text{SiO}_2$  and  $\text{FeO}$ ;  $\text{CaO}$  is undesirable with pyritic ore. The  $\text{SiO}_2$ - $\text{FeO}$ -content ought to be so proportioned as to furnish a slag which forms at a low temperature and requires little overheating to become fluid; the range of  $\text{SiO}_2$  lies between 15 and 25 per cent. The components of the charge must be well mixed.

**83. Examples of Up-draft Blast-roasting.**—The typical form of up-draft is represented by the Huntington-Heberlein pot shown in Fig. 155; a cast-iron pot *A* with detached hood, *C*, ending in off-take, *d*, which delivers gases into dust-flue, *e*; on the bottom the blast-pipe delivers air under baffle-plate, *g*, which so breaks the force of the blast that it may be evenly distributed by the perforations of arched sectoral cast-iron grate, *f*. In operating, a fire is made on the grate, protected by ashes or not, to ignite the charge which is to follow, or hot calcines are first introduced to serve the same purposes. The blast is started with the first fire; the ore to be roasted is introduced as fast as the roasting process started at the bottom will permit; the blast-gate is opened until the full blast is on. The charge is usually finished at full blast; often a reduced blast has been found preferable. The surface of the charge is kept open by punching; any blow-holes formed are closed by tamping.

At Garfield, Utah,<sup>2</sup> concentrates with 8 per cent. Cu and 30 per cent. S, rough-roasted in MacDougall furnaces to 17 per cent. S, were moistened with 5 per cent. water and blast-roasted in Huntington-Heberlein pots in 8-ton charges for 8 hr.; the blast-pressure of 6 oz. at the start was raised to 25 oz. and diminished toward the end to 20 oz. The roasted ore retained 6 per cent. S, but only

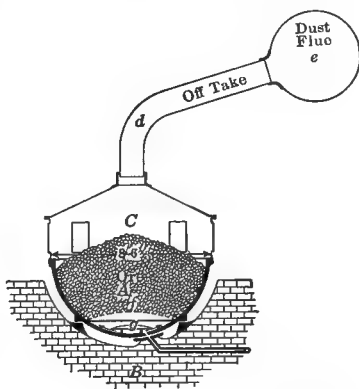


FIG. 155.—Huntington-Heberlein blast-roasting pot.

<sup>1</sup> Hofman, "General Metallurgy," 1913, pp. 411, 429.

<sup>2</sup> Hofman, *Tr. A. I. M. E.*, 1910, XL1, 750.

the lower half of the charge was sintered, the upper remaining pulverulent. The plant has been put out of commission.

At Morcenci, Ariz.,<sup>1</sup> sulphide copper ore and blast-furnace flue-dust were successfully blast-roasted by the Detroit Copper Co. in a spherical kettle, 9 ft. in diameter and 3 ft. deep to top of grate, holding 10 tons of charge made up of 8 tons concentrate ( $\text{SiO}_2$  14.3, Fe 24.9,  $\text{Al}_2\text{O}_3$  5.0, CaO 0.5, MgO 0.5, S 32.2, Cu 18.8 per cent.) and 2 tons of flue-dust ( $\text{SiO}_2$  23.9, Fe 25.9,  $\text{Al}_2\text{O}_3$  5.5, CaO 1.0, MgO 0.5, S 16.2, Cu 17.1 per cent.). A screen-analysis of the concentrate showed: > 0.5 in., 3.3 per cent.; < 0.5 and > 10-mesh, 9.6; 10- to 40-mesh, 30.9; 40- to 80-mesh, 25.5; 80- to 120-mesh, 14.0; 120- to 200-mesh 17.8; < 200 mesh, 8.9 per cent.

In starting, the grate was covered with ashes to a depth of 0.75 in., a fire was kindled at the center with the blast at 2 oz. pressure, then saw-dust was fed until about 6 in. deep at the center and tapering toward the periphery, and lastly 2 tons of warm (80° C.) flue-dust were charged to be followed by a 3-in. layer of concentrate. After 30 min. blowing, the concentrate was well kindled, the blast was turned on fully giving a pressure of about 18 oz., and the rest of the concentrate fed in as fast as the heat crept up. The time of a blow was 20 hr.; a charge furnished 93 per cent. coarse material with  $\text{SiO}_2$  17.6, Fe 34.5,  $\text{Al}_2\text{O}_3$  5.8, CaO 0.8, MgO 0.6, S 9.4, Cu 21.4 per cent. Metallurgically this work was satisfactory, as was that carried out later in a Dwight-Lloyd straight-line machine; but blast-roasting with blast-furnace smelting has had to yield to roasting in MacDougall furnaces and smelting in oil-fired reverberatories.

Neill records<sup>2</sup> the blast-roasting experiments he carried out at Mine La Motte, Mo., in 1883 with nickel-bearing pyrite, and his later work in Bingham cañon in 1894 or 1895 with sulphide copper ore from the Commercial mine; he illustrates the plant he built for the Yampa smelter, Utah, in 1903. The first experiments with blast-roasting are probably those recorded by Roswag,<sup>3</sup> which were made in Spain.

Collins<sup>4</sup> gives some facts about blast-roasting in a Spanish plant. The ore treated is a concentrate with from 15 to 18 per cent. Cu, and a mine fine with from 8 to 15 per cent. Cu. The mixture averages 15 per cent. S and receives from 5 to 6 per cent. fine iron ore; if it is sufficiently coarse, containing much 0.25-in. material, it is blown direct; if a large portion is finer than 8-mesh, about 3 per cent. slag is added to the ore.

Fig. 156 gives a vertical section of a Collins blast-roasting pot. The pot, A, is of mild steel and is enclosed by an open jacket filled with water to prevent overheating; the bottom is closed by a cast-steel wind-box, E, and a conical cast-iron grate, T, having 123 conical holes,  $\frac{3}{8}$  and  $\frac{5}{8}$  in. in diameter. The pot is supported by trunnions, C, on uprights, D, forming part of the carriage, B,

<sup>1</sup> Hofman, *loc. cit.*

<sup>2</sup> *Tr. A. I. M. E.*, 1910, XLI, 915.

<sup>3</sup> Frémy "Encyclopédie Chimique" Dunod, Paris, 1884, section I, vol. v, p. 243, and section II; *Eng. Min. J.*, 1902, XCII, 750.

<sup>4</sup> *Min. Mag.*, 1909, I, 52.



and is turned by worm and hand-wheel. The wind-box, *E*, is connected by a 6-in. alum-soaked canvas hose with an underground main. The gases are conducted away through a hood connected by a 3-ft. pipe with a dust chamber built of brick soaked in tar. A pot holds from 3400 to 3600 lb. charge.

In starting, glowing coals are introduced, a slight blast turned on, some fresh coal added, and about 100 lb. mixture charged. In about 10 min., when this primer has begun to glow, the pot is disconnected, moved to a loading platform, charged and returned to its place, when a blast with from 7 to 8 oz. pressure is turned on; this is then increased to 12-13 oz. A coarse charge requires from 6

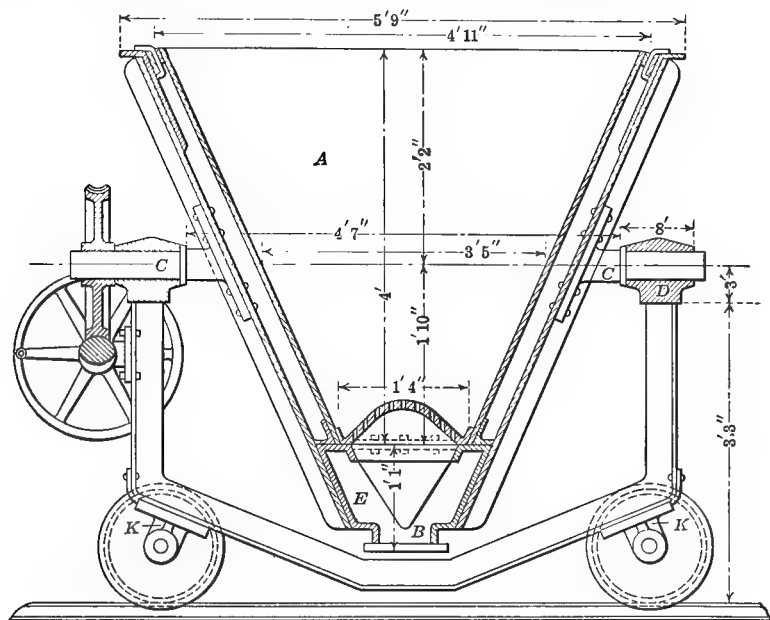


FIG. 156.—Collins blast-roasting pot.

to 7 hr. blowing, a fine charge from 9 to 10 hr. The sintered product, ordinarily from 90 to 95 per cent. of the whole, assays: Insol. 56.2, FeO 12.6, MnO 0.2, CaO 6.5, MgO 1.2, Al<sub>2</sub>O<sub>3</sub> 7.1, Cu 7.7, S 2.0, SO<sub>3</sub> 1.4, total S 2.6.

At the Wallaroo Works, South Australia,<sup>1</sup> blast-roasting in spherical pots, provided with hoods, mounted on trunnions and tipped by worm and hand-wheel, is in successful operation with ore, low-, and high-grade matte. The pot is 8 ft. 8 in. in diameter, 4 ft. 6 in. deep, has steep sides ( $14^{\circ}$  from vertical), and holds from 8 to 9 tons of charge; the grate, perforated by  $\frac{5}{8}$ -in. holes, is 10 in. above the bottom; the blast-pipe is 8 in. in diameter. The success depends to a large extent upon keeping down the temperature by the addition of abundant water; thus, ore requires 6-9, ordinary matte 4-6, rich matte 3-4 per cent.

<sup>1</sup> Cloud, *Tr. Inst. Min. Met.*, 1906-07, XVI, 311.

Austin, *Min. Ind.*, 1907, XVI, 335.

Radcliff, *Min. Sci.*, 1909, LIX, 67.

water. The tendency to reach an excessively high temperature is due to the combustion of Fe, causing premature fusion and thereby stoppage of roast. An ore-charge—made up of  $\frac{1}{3}$  coarse ( $1-1\frac{1}{4}$  in. in diameter) and  $\frac{2}{3}$  fine material—assays  $\text{SiO}_2$  15-35, S 15-25, Cu 10 per cent.; it is blown in from 8 to 12 hr., coarse working more quickly than fine. In operating the grate is protected by roasted pieces, 3-4 in. in size; the fire is started with wood and saw-dust and a slight blast. When the fire has extended from the center to the periphery, the pot is half filled with charge, the latter being piled up on the side where the blast tends to rise quickly. The blast is now increased, and 0.5-in. holes are punched in the surface. In 1 hr. the fire becomes visible around the center, when full blast (1000 cu. ft. per minute at 13 oz. pressure) is given. The blown cake, weighing about 6 tons, is dumped, lifted by a crane and dropped on to cast-iron cones. The cake retains 5-6 per cent. S. The converter-gases contain  $\text{SO}_2$  5.4, O 8 per cent. vol.

For blowing ordinary matte, this is crushed to  $\frac{1}{2}-\frac{3}{4}$  in., mixed with 15-25 per cent. siliceous ore, wetted, and charged into the pot gradually so as to cover the fire, as this appears on the surface until the pot is filled. The blast-pressure is 6-8 oz.; the issuing gas contains  $\text{SO}_2$  5.5, O 12 per cent. vol. Rich matte (white metal) is crushed to  $\frac{5}{8}$ -in. size, wetted, and blown without additions in pots, 5 ft. 3 in. in diameter at top, 11.5 in. at bottom and 3 ft. 6.5 in. deep, holding 2-ton charges. When the fire of wood and saw-dust has been started, lumps of roasted matte are introduced and brought to a red heat; the pot is half filled with matte and blown with a pressure of 6 oz., then completely filled. After the fire has appeared on the surface, the charge is blown with a pressure of 8 to 10 oz., a blow lasts 8-10 hr. The dumped cake, which consists of a mixture of sulphide, oxide, and metal, is broken by an iron ball weighing 1600 lb. and dropping 20 ft.

The converter-gases average  $\text{SO}_2$  11.1, O 5.6 per cent. vol.

As to the elimination of impurities in treating white metal, blast-roasting gives 1.87 per cent. Ni and 1.39 per cent. Bi; when the Direct or Nichols-James process (§ 153) shows 1.5 per cent. Ni and 1.12 per cent. Bi; and roast-smelting (§ 153) 1 per cent. Ni and 1 per cent. Bi.

At Blagodatny<sup>1</sup> matte is blast-roasted in a conical tilting pot, 3.28 and 4.01 ft. in diameter and 4.687 ft. in height, with central perforated air-delivery pipe extending to near the top, in charges of 3600 lb. (5.66 matte : 1 siliceous concentrator tailing) in from 30 to 35 hr.; the product retains S 12-13 per cent.

At the Casapalca smelter, Peru,<sup>2</sup> ore with  $\text{SiO}_2$  25, Fe 15.6,  $\text{Al}_2\text{O}_3$  3.8, CaO 9, Zn 11.1, S 24.4, Pb 6, Cu 3.5 per cent., and Ag 44 oz. per ton, is crushed to pass a 3-in. screen, mixed with siliceous material and lime, moistened with 5 per cent. water, and blown in a Savelsberg pot. This is 8 ft. 8 in. at the mouth, where it is 2 in. thick, and tapers to  $1\frac{1}{8}$  in. at the bottom; the height from grate to rim is 3 ft. 6 in., that from rim to center of trunnion 2 ft. (= 2 in. below center of gravity of charged pot). The inside of the pot has four rings,  $\frac{7}{8}$  in. wide, to counteract

<sup>1</sup> *Metall-Erz.*, 1913, X, 612.

<sup>2</sup> Strauss, *Min. Mag.*, 1911, V, 59.

creeping up of blast. The grate,  $1\frac{1}{8}$  in. thick, is arched to a radius of 11 ft.; it consists of a center and two side-pieces, stands 14 in. above the bottom, and rests upon shoulders, 1 in. wide, bolted to the outside of the pot. The air-holes, 1 in. in diameter at inlet and  $\frac{3}{8}$  in. at outlet, are  $2\frac{1}{4}$  in. apart. The blast-pipe is 6 in. in diameter; the conical hood has one feed and seven working doors; it enters a telescope stack 30 in. in diameter, and is raised and lowered by a hand-wheel. The pot is tilted by a worm gear, the carriage is held by a wire rope on its slightly inclined track. A full charge weighs 9 tons. The fire is started with shavings and wood to a depth of 3-4 in., blast is turned on, 100 lb. coke breeze ( $< \frac{3}{4}$  in.) are charged, a layer of limestone is given, and 1200 lb. ore are shoveled in in three charges, each being spread with a rake; the blast is correspondingly increased. The rest of the charge is dropped through a chute from an overhead hopper, in lots of 800 lb. and more at a time; the surface of the charge is kept open by punching. When the full charge has been given, the blast shows a pressure of 5.5 oz., and rises to 9 and 10 oz. toward the end of the 11-hr. blow. The desulphurization reaches 75 per cent., the loss in weight is 10 per cent.; little flue-dust is made. A sample of sinter-cake gave  $\text{SiO}_2$  28.6, Fe 15.8,  $\text{Al}_2\text{O}_3$  3.9, CaO 10.6, Zn 10.8, Cu 4.1, S 6.1, Pb 5.4 per cent., Ag 48 oz. per ton.

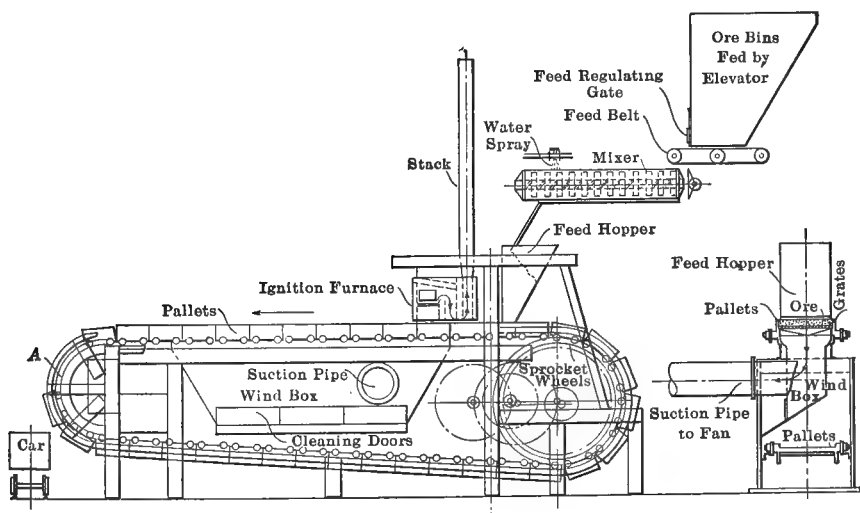


FIG. 157.—Dwight-Lloyd straight-line roasting machine.

**84. Examples of Down-draft Blast-roasting.**—The leading apparatus is the Dwight-Lloyd straight-line roasting machine,<sup>1</sup> shown in Fig. 157. It consists of a frame of structural steel supporting a feeding-hopper, an igniting furnace, a suction-box, and a pair of endless-track circuits to accommodate a train of small truck-like elements called pallets which, in combination, form practically an endless conveyor, with the continuity broken at one place in the

<sup>1</sup> Hofman, *Tr. A. I. M. E.*, 1910, XLI, 759, "General Metallurgy," 1913, p. 430.

circuit. Each pallet is provided with four wheels, which engage with the tracks or guides at all parts of the circuit, except when the pallet is passing over the suction-box, and then the pallet slides on its planed bottom over the planed top of the suction-box, thus making an air-tight joint. A pair of cast-steel sprocket-wheels, turning inside of concentric guide-rails, lift the train of pallets from the lower to the upper track by engaging their teeth with the roller-wheels, and launch each pallet in a horizontal path under the feed-hopper and igniting-furnace, and over the suction-box. In a train of pallets in action, all the joints are kept closed, and air-tight, by the pallet being pushed from behind. At the beginning and the end of the track formed by the planed top of the suction-box, there is a planed "dead-plate" over which the pallets must glide; it serves to prevent any leakage of air. After a pallet passes over the suction-box and terminal dead-plate, its wheels engage the ends of the circular discharge-guides. These are adjusted with the view of raising the pallet about 0.5 in. vertically and thus automatically prying up the cake of sinter and freeing it from the grate-slots. A "breaking-roller" prevents the prying action from extending too far back, and tends to form a line of fracture. This roller, however, is not essential in all cases. On reaching the curve of the guides, the pallets one by one drop into the guides, each strikes the pallet which has preceded it and, at the same time, discharges its load of sinter-cake, and shakes free the slots of the grates. The force of the blow can be regulated by the gap left in the train of pallets at this point. The weight of the train keeps the pallets fed down to the lower teeth of the sprocket-wheels.

The igniter frequently used with this machine is a small coal-burning furnace built of tiles, having a grate-area of 10 by 30 in. and burning 500 lb. of coal in 24 hr. The flame after passing over the fire-bridge is deflected downward upon the ore by a brick curtain that can be raised and lowered, and then is drawn upward by the natural draft of a small stack or bleeder.

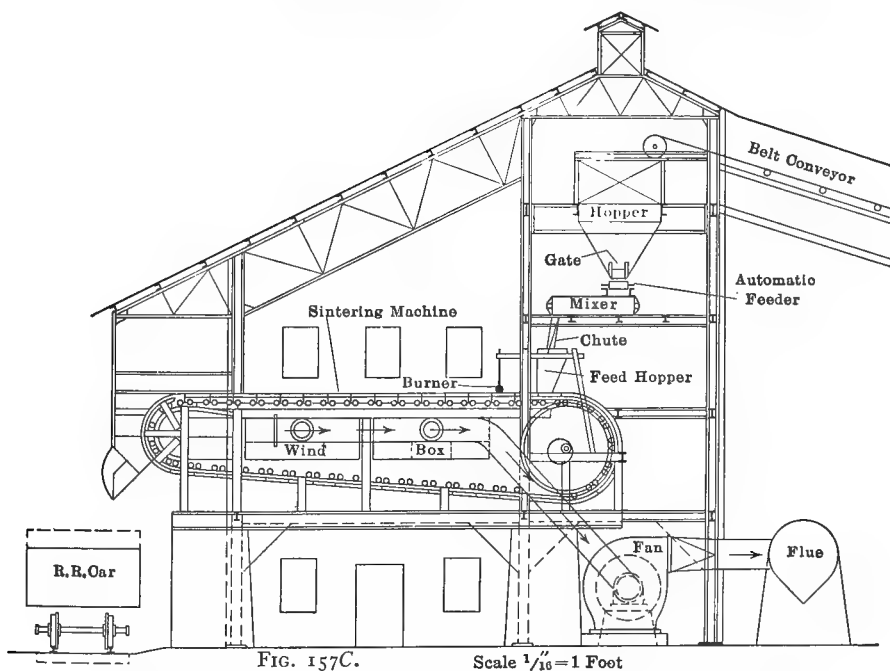
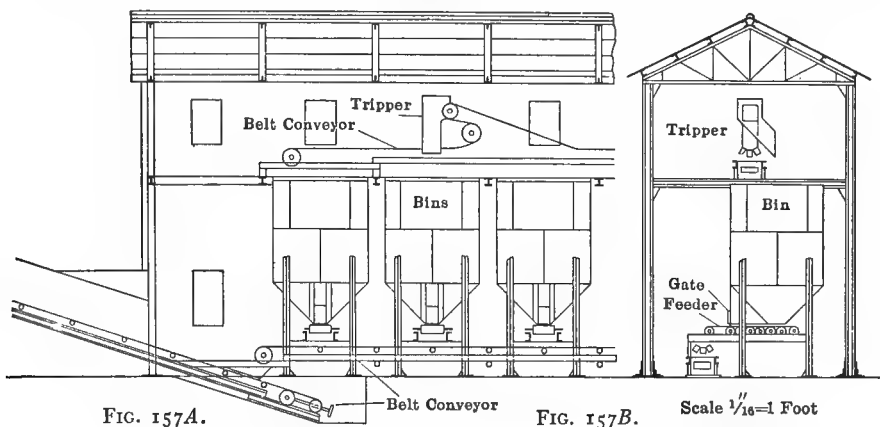
The suction-box on top is 12 ft. 6 in. long and 30 in. wide, and gives for the grates an effective hearth-area of 31.25 sq. ft.; this is the true measure of the capacity of the machine. The pallets are each 30 in. wide by 18 in. long and weigh with grates 550 lb.

The power delivered to the machine has its speed-factor reduced by passing through a train of gear-wheels, the last of which engage the internal gear-teeth cast in the large sprocket-wheels, and actuate the train of pallets.

The complete cycle of operations is as follows: A pallet, being pushed onward tangentially from the top of the sprocket-wheels, passes under the feed-hopper, where it takes its load in the form of a continuous even layer of charge, say 4 in. thick, passes next under the ignition-furnace, where the top surface is kindled, and at the same time comes within the influence of the downward-moving currents of air, induced by the suction-draft; these carry the sintering action progressively downward until it reaches the grates. The roast-sintering operation is complete, the cake is discharged by dropping into the discharge-guides, and the pallet crowds its way back to the sprocket-wheels, is slowly raised to the upper tracks, and begins a new cycle.

A straight-line machine of the size described with effective area of 31.25 sq. ft. weighs, without accessories, approximately 16 tons.

The general arrangement of a Dwight-Lloyd sintering plant has gradually



FIGS. 157 A, B, C.—Plant of Dwight-Lloyd straight-line roasting machine.

taken a standard form of which a diagrammatic sketch is given in Fig. 157 A, B, and C.<sup>1</sup> The ores to be blast-roasted arrive on a belt-conveyor, Fig. 157

<sup>1</sup> Drawings of plant of Ohio and Colorado Smelting & Refining Co., Salida, Colo., *Met. Chem. Eng.*, 1912, x, 87.

A and B, on the top floor of the building containing the mixing bins and are discharged by means of a tripper into the cylindrical hopper-bottom bins. The content of each of these bins is discharged in the desired amount by its traveling belt through a regulating gate on to a main belt conveyor which delivers on to an inclined belt conveyor raising the unmixed charge components to the feed-hopper on the top of the roaster-building, Fig. 157 C. This holds the charge, now mixed somewhat, but insufficiently to furnish a uniform product. This is obtained in the mixer, which receives its material from the hopper through an automatic feeder and gate, and discharges the uniform material through a chute into the feed-hopper of the machine proper. By this arrangement the handling and mixing of the ores as well as the blast-roasting have become entirely mechanical, and require only attendance for overseeing.

In blast-roasting sulphide copper ores at Cerro de Pasco, Peru (14,000 ft. elevation), Lloyd<sup>1</sup> found that the ignition flame had to be hotter than at lower altitudes, that charges could be worked with as high a S-content as 25 per cent., and that the process proceeded a little more slowly. He also states that the flowers of sulphur and dust from pyritic ore, which collect in the fan and have to be removed at intervals, show no tendency to self-ignition or to forming explosive mixtures.

At Trail, B. C.,<sup>2</sup> producer gas is used for igniting the 60-mesh concentrate which contains Cu 1, Fe 3, SiO<sub>2</sub> 40, Al<sub>2</sub>O<sub>3</sub> 15, CaO 1.5, S 15.5 per cent. and Au 1 oz. per ton. From 30 to 35 tons are treated by a machine in 24 hr. with a reduction of the S-content to 1.0-1.5 per cent. According to Jacobs<sup>3</sup> the herring-bone grate of the standard machine has been replaced by one with straight slots.

A mechanical cleaner<sup>4</sup> has been devised which eliminates the man required to remove from the grates adhering particles of blast-roasted material.

At Plant A, a 42- by 264-in. machine, with pallets moving at a speed of from 12 to 24 in. per minute, treats a mixture of siliceous sulphide ore (Cu 6-10, Fe 15, SiO<sub>2</sub> 55, CaO 2, S 10 per cent.), sulphide concentrate (Cu 12, Fe 24, SiO<sub>2</sub> 30, S 25 per cent.), and pyrite cinder (Cu 2.5, Fe 54, SiO<sub>2</sub> 8, S 2.5 per cent.), all passing through a  $\frac{1}{4}$ -in. screen and 10 per cent. through a 40-mesh sieve, at the rate of 90-110 tons in 24 hr.; crude oil is used as igniter.

At Plant B, a 42- by 264-in. machine, with pallets moving at a speed of from 20 to 36 in. per minute, treats flue-dust (SiO<sub>2</sub> 22-30, Fe 25-29, Al<sub>2</sub>O<sub>3</sub> 10-17, Cu 6.5-8.5, CaO 1.5, total S 5-16, sulphate -S 1-5.5, high in As<sub>2</sub>O<sub>3</sub>) of which 26 per cent. passes through a 100-mesh sieve and 90 per cent. of the 100-mesh material through a 200-mesh sieve, at the rate of 100-120 tons in 24 hr., producing a sinter, usually all coarse, with 1-2 per cent. S.

The former work at the plant of the Tennessee Copper Co. is recorded by Smith.<sup>5</sup> The treatment of flue-dust at Mason Valley is discussed in § 122.

<sup>1</sup> *Min. Sc. Press*, 1913, VII, 908.

<sup>2</sup> J. Buchanan, Sept., 1913.

<sup>3</sup> *Canad. Min. J.*, 1913, XXXIV, 518.

<sup>4</sup> *Eng. Min. J.*, 1913, XCVI, 789.

<sup>5</sup> *Min. World*, 1910, XXXIII, 460.

**85. Summary of Roasting.**<sup>1</sup>—The apparatus discussed in § 55–84 represent the leading types that have been or are in use at various industrial plants. Quite a number would probably not be built again for new plants. Thus, heaps will be used only, if the ore is not suited for pyritic or partial pyritic smelting as is the case with Ontario nickel copper ores; coarse ore-kilns will be confined to roasting in connection with the utilization or rendering harmless of sulphurous gases. Of the fine-ore kilns, those of the MacDougall type have proved on the whole to be more satisfactory than the others. Mechanical reverberatory furnaces will also be replaced in time by MacDougall furnaces run with auxiliary fire-places. Blast-roasting is confined to localities in which large modern reverberatory matting furnaces are not practicable. As regards matte, blast-roasting promises to be more satisfactory than the customary reverberatory-roasting for subsequent blast-furnace smelting.

Fine-ore mechanical roasting furnaces make much flue-dust, especially those having super-imposed hearth, such as the MacDougall. As most silver-bearing ores usually contain some arsenic, the gases from furnaces roasting them will be charged with  $\text{As}_2\text{O}_3$ .

Thus the dust-free gases from a MacDougall plant<sup>2</sup> contained at standard conditions:  $\text{SO}_2$  2.545,  $\text{SO}_3$  0.275,  $\text{CO}_2$  0.1136,  $\text{H}_2\text{O}$ -vapor 2.784,  $\text{As}_2\text{O}_3$  0.073, O 14.02, N 81.18 per cent. volume. Dust as well as vapor can be collected as long as the velocity and temperature of the gas-current are sufficiently reduced, and the time necessary be given for settling. A current-velocity of 6 ft. per sec. permits the collection of practically all suspended particles; for the complete condensation of vapor and of  $\text{As}_2\text{O}_3$  the temperature of the gases must be reduced to  $143\text{--}144^\circ\text{C}$ .<sup>3</sup>

A screen-analysis of real flue-dust from Great Falls, Mont.,<sup>4</sup> showed that it was finer than 0.5 mm.; considering that at this plant 55 per cent. of the material charged into a MacDougall furnace is smaller than 0.5 mm., this furnace will produce a large part of the total made at the works.

The method ordinarily employed in the copper smelteries of the United States to clean roaster-gases is to have them travel through a dust chamber and then through long flues before they enter the stack. The flue-system of the MacDougall furnaces at Cananea has been shown in Figs. 99, 107, and 108. At Anaconda the roaster gases travel 3017 ft. at a decreasing velocity. The research of Dunn<sup>5</sup> has shown that all the dust and most of the fume are settled. At Great Falls, after an exhaustive study of the subject of condensation by Goodale,<sup>6</sup> the Roesing wire-system was introduced, which has proved itself to be very efficient.

The question of condensation of flue-dust in copper-plants will be discussed in § 122.

<sup>1</sup> See also Dwight, *School Min. Quart.*, 1911, XXXIII, 1; *Eng. Min. J.*, 1911, XCII, 1267.

<sup>2</sup> Dunn, *Tr. A. I. M. E.*, 1913, XLVI.

<sup>3</sup> Elton, *op. cit.*, 1913, XLVI.

<sup>4</sup> Goodale, *op. cit.*, 1913, XLVI.

<sup>5</sup> *Tr. A. I. M. E.*, 1913, XLVI.

<sup>6</sup> *Tr. A. I. M. E.*, 1913, XLVI.

## II. SMELTING IN THE BLAST-FURNACE

**86. The Blast-furnace and Its Accessory Apparatus in General.**<sup>1</sup>—The blast-furnaces in operation in the United States in copper smelting resemble one another so much that they are approaching standard forms, whether a reducing or a pyritic fusion is carried on; in fact they are the outcome of furnaces developed at Great Falls, Mont.<sup>2</sup> They differ greatly from those in operation 25 or 30 years ago. The earlier furnaces were copies of European models.<sup>3</sup> At first they were built of stone and brick, were square, and had a single tuyère-pipe at the back; later they were made slightly oblong and had two or three tuyères at the back. When the greatest length with this arrangement of air-supply had been reached, tuyères were added at the sides, and the width of the furnace was increased. In order to protect the walls of the old furnaces, blown from the back, against fusion and corrosion, the fuel used to be charged toward the front and ore with flux toward the back; smelting thus took place in the center of the furnace. With the advent of tuyères on four sides, the brick walls were protected by having water-cooled tuyères project beyond them into the furnace, when the blast passing through the nozzles would strike the carbonized fuel several inches away from the wall and cause the hottest zone to prevail nearer the center than the wall. The transition from water-cooled tuyère to water-cooled smelting-zone and later to water-cooled furnace was gradual.

At present most copper blast-furnaces for smelting sulphide ore are water-cooled throughout, as almost every furnace-man works for some pyritic effect in order to oxidize part of the S and Fe in the charge. He accomplishes this in part by forcing into the furnace a large volume of air, or by having a low charge-column, or by both means. The result is that usually the heat creeps up and the top becomes hot. With the upper part of the shaft built of brick, the wall-corrosions or -accretions would become unmanageable, hence the water-cooled shaft, and sometimes even water-cooled parts above the feed-floor. In a strictly reducing fusion, in which the smelting zone reaches only a short distance above the tuyères, the upper part of the shaft is of brick, as this material abstracts less heat than a water-cooled jacket. Water-jackets at present are nearly always of soft steel, as their large sizes preclude the use of the cheaper cast iron, Mount Lyell, Tasmania, forming the leading exception.

The furnaces are all oblong with tuyères on the sides, as with a given limiting distance between tuyères the length can be adapted to the desired capacity. The vertical section of an oblong furnace shows that the ends are usually vertical; and that the sides either taper uniformly from throat to bottom, or only the

<sup>1</sup> Mathewson, *Eng. Min. J.*, 1911, XCI, 1057.

<sup>2</sup> Church, *Tr. A. I. M. E.*, 1913, XLVI, 423.

<sup>3</sup> General Treatises on Metallurgy of Balling, Kerl, Schnabel-Louis, and others.

Wendt, *School Min. Quart.*, 1885-86, VII, 174, 181, 304, 314 (Alleghanies).

Egleston, *Tr. A. I. M. E.*, 1881-82, X, 25 (Ore Knob), *School Min. Quart.*, 1885-86, VII, 360 (Point Shirley, Boston).

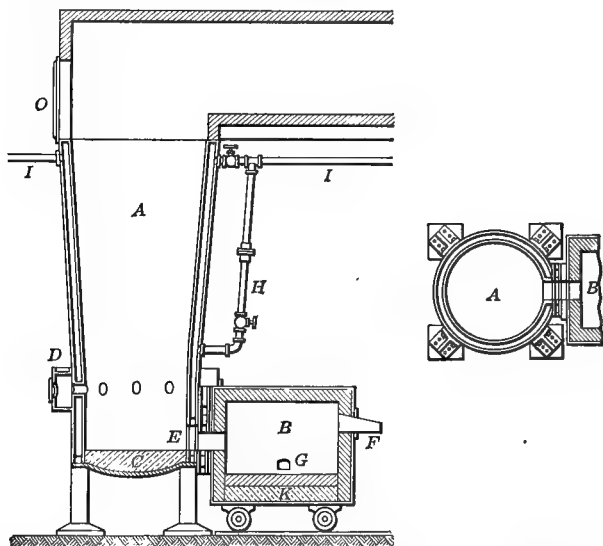
Tables in *Metallurgie*, 1905, II, 417; 1907, IV, 104.



lower sides enclosing the smelting zone taper, while the upper are vertical. The amount of bosh thus given is governed by the reducing effect to which the charge is subjected; the greater the angle of bosh, the stronger the reduction.

All furnaces have a detached external crucible, and this is either fixed or movable. The disadvantages of loss of heat and thereby of imperfect separation of matte from slag, characteristic for external crucibles of small furnaces, have been overcome in large furnaces by the large stream of molten material which often keeps the fore-hearth so hot as to necessitate water-cooling in order to prevent matte from breaking through the lining. The fore-hearth has grown with the size of the furnace, and sufficiently so to become a reservoir of matte for the converter. Little need be said from a general point of view about the accessory apparatus, such as slag-pots, matte-pots, etc.

**87. The Blast-furnace in General.**—The Great Falls, the Anaconda, the Cananea and the Mount Lyell furnaces, which are the outcome of the furnace developed by F. Klepetko at Great Falls,<sup>1</sup> showing the leading points of a modern copper blast-furnace, are discussed in § 90.



FIGS. 158-159.—Herreshoff circular water-jacket blast-furnace with detached fore-hearth.

**88. The Herreshoff Furnace.**—The prototype of this furnace is the circular furnace designed by J. B. F. Herreshoff,<sup>2</sup> for the Nichols Copper Co., Brooklyn, N. Y., and shown in Figs. 158-159. The shaft, *A*, consists of a double shell of boiler-plate, 10 ft. high, 4 ft. inner diameter at tuyères and 5 ft. 6 in. at throat, with a 2-in. water-space, water-inlet and outlet pipes, *H* and *I*, and hand-holes, not shown, for removal of sediment.

At the bottom the shells are connected by rivets passing through a wrought-

<sup>1</sup> Church, *Tr. A. I. M. E.*, 1913, XLVI, 423.

<sup>2</sup> McDowell, *Tr. A. I. M. E.*, 1884-85, XIII, 124.

iron ring 4 in. wide; at the top the inner shell is turned outward 4 in. to overlap the outer, similarly bent, and the two laps are riveted together. The bottom, *C*, is a shallow cast-iron basin bolted to the ring connecting the inner and outer shells of the jacket. It is supported by four hollow cast-iron columns, 2 ft. 6 in. high. The working-bottom is made up of a mixture of crushed fire-brick and raw clay rammed down, to be level with the discharge, and to rise slightly toward the opposite side. The blast is supplied by a No. 5 Roots blower to the air-box, *D*, 20×4 in., which extends around the furnace except for one-sixth of the circumference. The blast passes through four 2-in. tuyères into the furnace; opposite each tuyère is an opening in the outer wall of the air-box, closed by a removable cover with peephole, for inspecting and poking.

The detached fore-hearth is a rectangular box on wheels made up of ribbed cast-iron plates bolted together. The bottom is lined with slag-wool and fire-brick, the sides with fire-brick alone; the cover consists of a number of iron-clamped fire-brick arches. At the discharge-end near the top is the slag-spout, at one side near the bottom the matte-tap. The water-jacketed inlet for the slag-matte, 7×6 in., is placed 12 in. above the brick bottom and below the slag-outlet in order that the melted mass may trap the blast. A close contact between fore-hearth and furnace is obtained by flattening the latter at the discharge. A tight joint is formed by slag chilling around the two water-cooled surfaces which have been coated and luted with clay. During the run, the slag-matte runs continuously from the furnace into the fore-hearth where the two separate. The slag overflows continuously into a slag-pot; the matte is tapped periodically in such quantities that the slag in the fore-hearth will not sink beneath the inlet and allow the blast to issue forth. If the fore-hearth should become too cool, enough matte is tapped to allow this to take place and thus heat the hearth. Should this not remedy the evil, or should the hearth become choked, the water-connections are severed, and a clean heated hearth put in its place. This furnace treated in a straight reducing fusion in 24 hr. about 60 tons of charge (52 per cent. roasted pyrite, 5 raw pyrite, 3 sand) using 20 per cent. gas coke.

A similar furnace,<sup>1</sup> elliptical in cross-section, 3 ft. 7 in.×6 ft. 4 in. at tuyères, 4 ft. 7 in.×7 ft. 4 in. at throat, 10 ft. high, 13 tuyères 2 in. in diam., 26 in. above bottom-plate, outlet 9×7 in., with circular fore-hearth, water-jacketed on sides, lined with one course of brick, put through in 24 hr. 95 tons of charge (77 per cent. roasted pyrite, 13 raw pyrite, 5 sand) with 18 per cent. gas coke and 12 oz. blast. Its former work with copper-nickel ores at Copper Cliff, Ont., is given by Levat.<sup>2</sup> The present furnace of the Nichols Copper Co., is noted in Table 28.

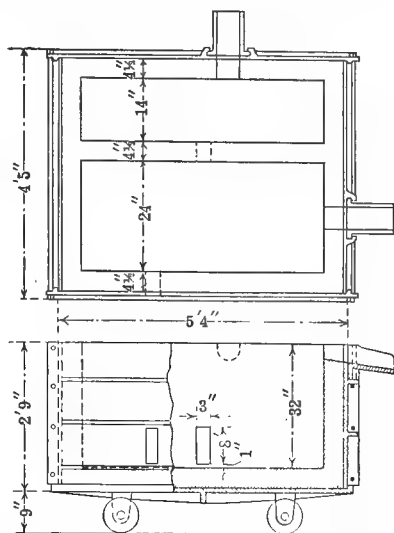
THE ORFORD FORE-HEARTH, designed by H. M. Howe in 1879, which separates and continuously discharges both matte and slag, may be noticed in connection with the Herreshoff furnace. One form is given in Figs. 160-161,<sup>3</sup>

<sup>1</sup> Wendt, *loc. cit.*

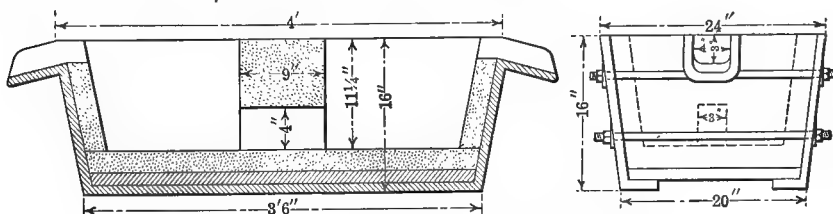
<sup>2</sup> *Ann. Min.*, 1892, I, 170.

<sup>3</sup> Peters, "Modern Copper Smelting," 1901, p. 294.

which represent, a movable oblong box of ribbed cast-iron plates, fastened together with hooks and eyes and tied with iron rods; the top is open; there is no inlet in the end, nor a matte-tap in the side. A vertical partition wall of fire-brick, 9 in. thick, divides the fore-hearth into two unequal compartments the areas of which are as 2 : 5; communication between the two is established through a slot,  $3 \times 8$  in., near the bottom of the wall. In starting, the fore-hearth, dried and heated with the slot closed by a clay plug, is rolled in front of the furnace with the larger receiving compartment facing the spout over which the slag-matte flows. This enters the larger compartment and fills it, matte settles and collects on the bottom while the slag overflows into a waste-slag pot. When enough matte has collected in the compartment to appear at the slag-overflow, the plug in the communicating slot is pierced by a bent bar, whereupon matte alone will flow into the smaller compartment. Both compartments will now be slowly filled, the smaller one with matte, the larger one with matte overlain by slag; slag will overflow continuously from the larger compartment and matte from the smaller, the matte-spout being laid 2 in. lower than the slag-spout. The top is kept covered with burning wood and charcoal to prevent chilling. A furnace must produce at least 50 tons slag-matte in 24 hr. to allow using the fore-hearth. Matte with under 30 per cent. Cu. gradually eats away the partition-wall; matte with 50 per cent. Cu and over is likely to choke the slot.



FIGS. 160-161.—Orford original fore-hearth.



FIGS. 162-163.—Orford improved fore-hearth.

An improved form of this fore-hearth is shown in Figs. 162-163. This again is an oblong box of cast-iron plates lined with fire-brick, having a cross-partition with a  $3 \times 4$ -in. slot. The distance from bottom to slag- and matte-spouts is the same; the difference in level is obtained by placing the box on an inclined plane.

The overflow-slag from both forms of fore-hearth has to pass one or more settling-boxes or pots to give entrained matte the time necessary for complete separation. The fore-hearth is better adapted for matte-concentration than for ore-smelting, as with much matte there is formed a slag usually too rich in Cu to be discarded. However, the Hall Mining and Smelting Co.,<sup>1</sup> the Tyee Copper Co.,<sup>2</sup> and the Copper Queen Mining Co., at one time had adapted the principle of continuous matte-discharge to their ore-furnaces.

**89. Blast-furnace Buildings.**—Every blast-furnace building has at least three floors, the feed-floor, the furnace-floor, and the slag or matte-floor. They are shown clearly in Fig. 164, representing the furnaces of the Shannon Copper Co. The details of the feed-floor vary with the manner of delivering the charges to the furnace; the distance between the feed- and furnace-floors is governed by

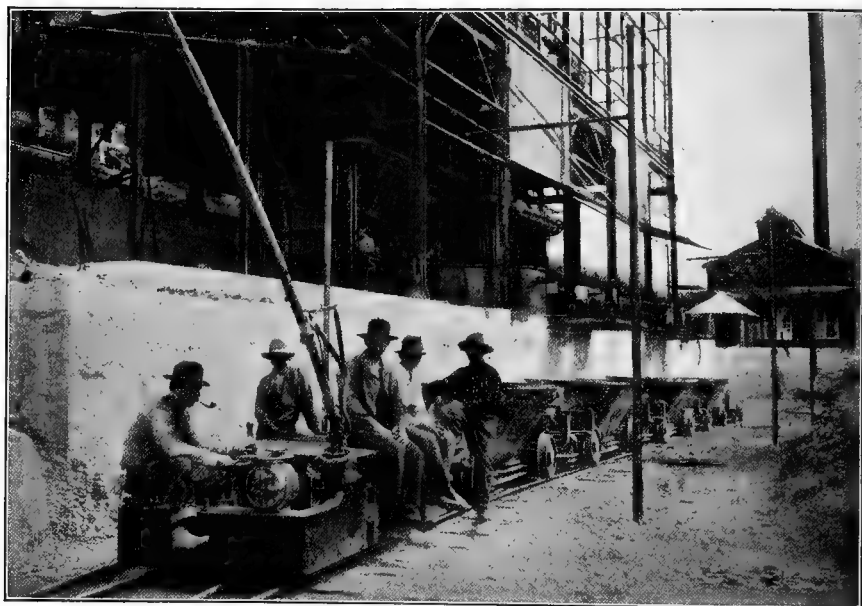


FIG. 164.—Blast-furnaces Shannon Copper Co.

the height of the furnace; the slag- or matte-floor has to be a sufficient distance (10 ft. more or less) below the furnace-floor to admit waste-slag cars holding from 5 to 15 tons of slag, and the matte-cars or matte-receiving ladles with a capacity of say 10 tons. If the slag is granulated, special provision has to be made to carry away the granulated material.

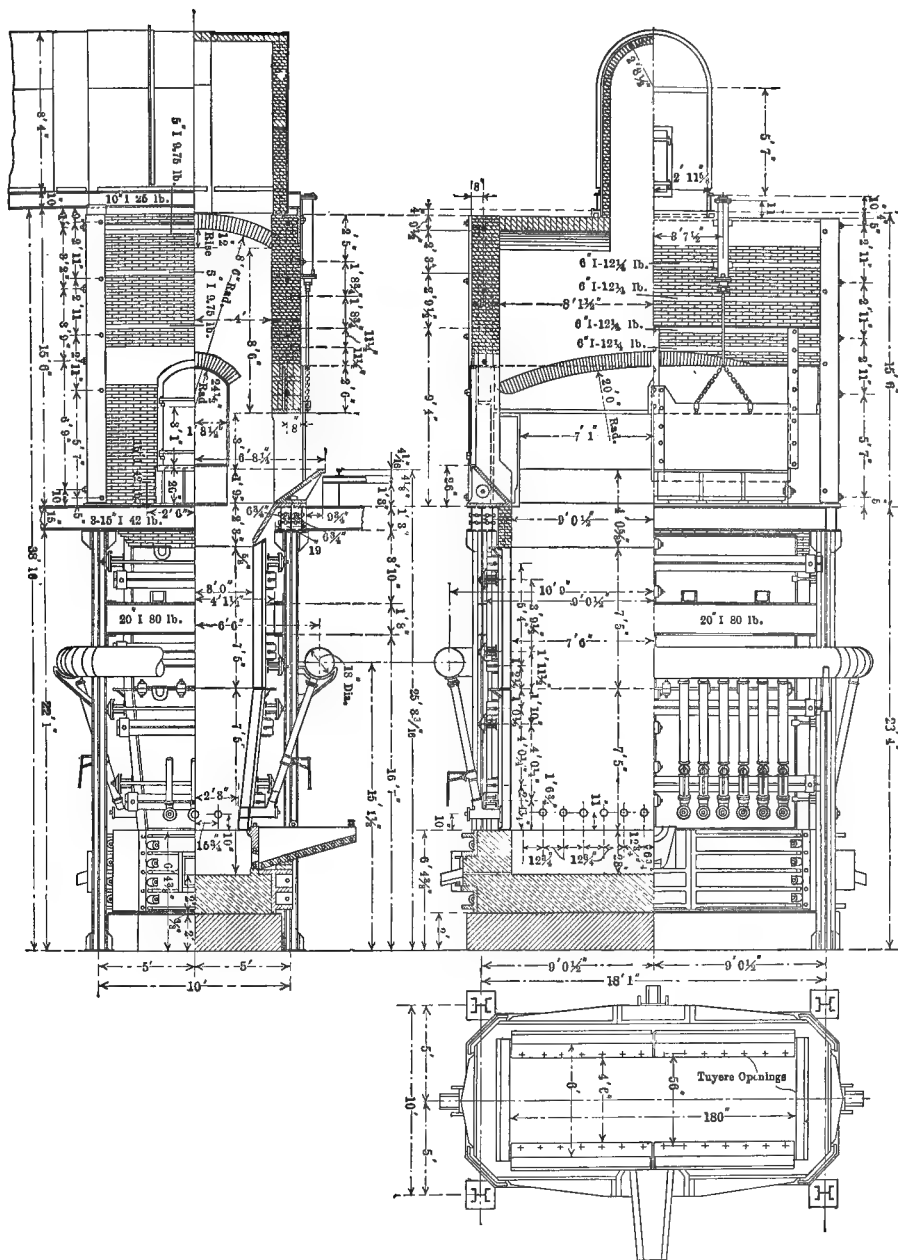
**90. Great Falls, Anaconda, Cananea and Mount Lyell Blast-furnaces.**—The Great Falls or Klepetko, Figs. 165-167,<sup>3</sup> the New Anaconda or Mathewson,

<sup>1</sup> Harris, *Eng. Min. J.*, 1906, LXXXI, 178.

<sup>2</sup> Jacobs, *op. cit.*, 1909, LXXXVII, 1232.

<sup>3</sup> Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 283.

Church, *op. cit.*, 1913, XLVI, 423.



FIGS. 165-167.—Great Falls or Klepetko blast-furnace.



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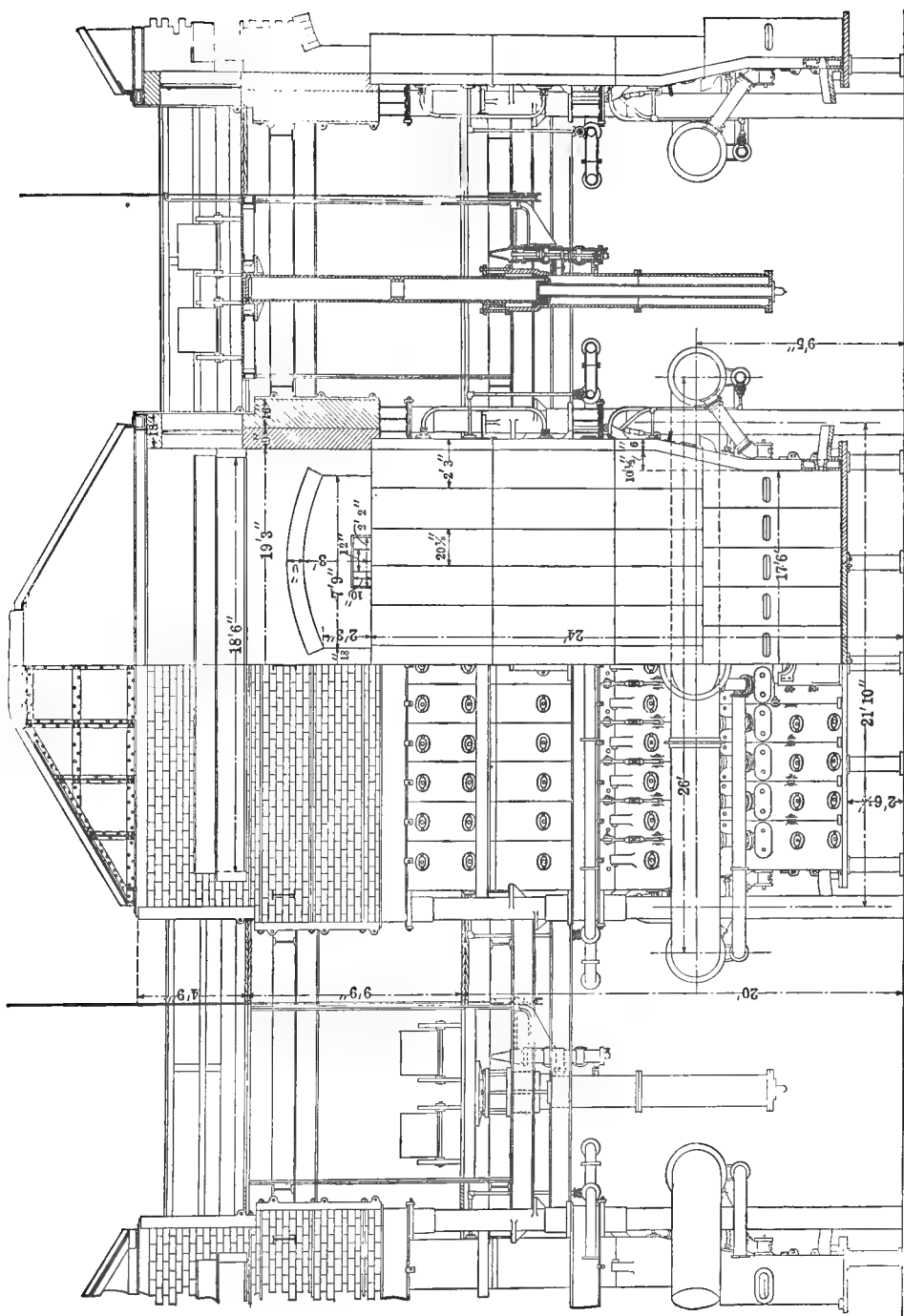


FIG. 175.—Mount Lyell or Sticht blast-furnace.



Figs. 168-170,<sup>1</sup> the Cananea or Shelby, Figs. 171-172,<sup>2</sup> and the Mount Lyell or Sticht, Figs. 173-174,<sup>3</sup> furnaces represent the modern forms of blast-furnaces.

They have this in common: they are oblong, have vertical ends, sloping or boshed sides with the necessary tuyères, a shallow crucible which discharges slag-matte mixture continuously over a raised spout trapping the blast (first used by R. H. Sticht), a large fore-hearth for separating and collecting matte, to be tapped periodically from slag overflowing continuously into a slag car or a granulating device. Only the leading features will be briefly reviewed; the details and those of some other important furnaces are assembled in Table 28.

**91. The Hearth.**—This is sometimes built up solid from the concrete foundation, Figs. 165-167; in most plants it is erected on ribbed cast-iron plates supported by iron posts and jack-screws, Figs. 171-174;<sup>4</sup> the latter are sometimes carried by a steel truck. With the new Anaconda furnaces, Figs. 168-170, both arrangements are found, the center division being carried by jack-screws, the end-divisions built up solid. The masonry of the hearth is encased by heavy ribbed cast-iron plates firmly bolted together. The jacked cast-iron bed-plate supporting the bottom of the hearth usually also carries the jackets; in this case the water-cooled side-walls as well as the air-cooled bottom are made thinner than with the hearth erected upon concrete, *e.g.*, side 22 in. and bottom 18 in. thick *vs.* 14 and 9 in. Sometimes the bottom-plates of the hearth contain pipe-coils for water-cooling. The refractory material used for lining used to be exclusively fire-brick. The corrosive action of hot matte not too high in Cu has been in many cases the cause of replacing fire-brick by silica-brick or chrome brick.<sup>5</sup> An analysis of the chrome brick used at Garfield gave:  $\text{Cr}_2\text{O}_3$ ,  $\text{SiO}_2$  6.9,  $\text{FeO}$  14.0,  $\text{CaO}$  0.5,  $\text{MgO}$  17.0  $\text{Al}_2\text{O}_3$  11.6. The brick, usually laid both end- and side-wise, are stepped down from near the level of the tuyères to the bottom and give the crucible a trough-like shape.

The trapped spout<sup>6</sup> for the continuous flow of slag-matte is situated at one side, Figs. 165-167, or one end, Fig. 174; sometimes there are spouts at both ends. For emptying the furnace, there is a tap-hole, sometimes water-jacketed, at the lowest point of the crucible or in the spout.<sup>7</sup> With the new Anaconda furnace, Figs. 168-170, having a tuyère-section  $56 \times 612$  in., the bottom of the hearth slopes from the center toward the ends, where are situated crucibles from the deepest points of which the slag-matte flows out at one side over two

<sup>1</sup> Mathewson, *Eng. Min. J.*, 1906, LXXXI, 370.

Austin, *Tr. A. I. M. E.*, 1907, XXXVII, 442.

Offerhaus, *Eng. Min. J.*, 1909, LXXXVIII, 243.

<sup>2</sup> Shelby, *Eng. Min. J.*, 1908, LXXXV, 841.

<sup>3</sup> Sticht, *Metallurgie*, 1906, III, 766;

Private Communication, 1911.

<sup>4</sup> See also Mather, *Tr. A. I. M. E.*, 1903, XXXIII, 675.

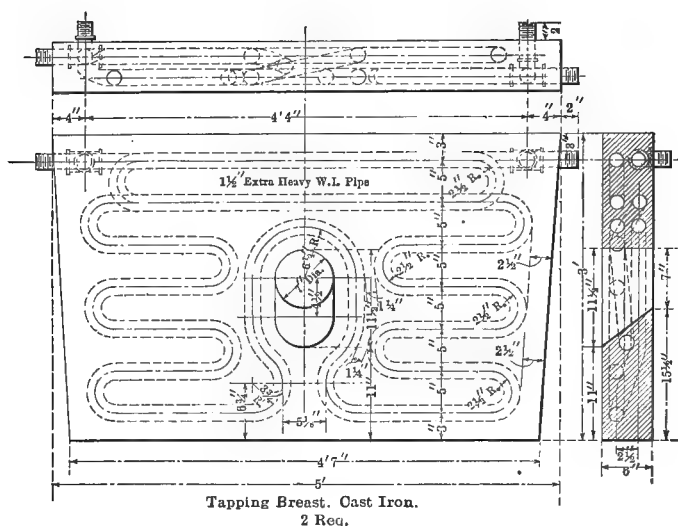
<sup>5</sup> Lang, *Eng. Min. J.*, 1897, LXIII, 89.

Packard, *op. cit.*, 1897, LXIII, 159.

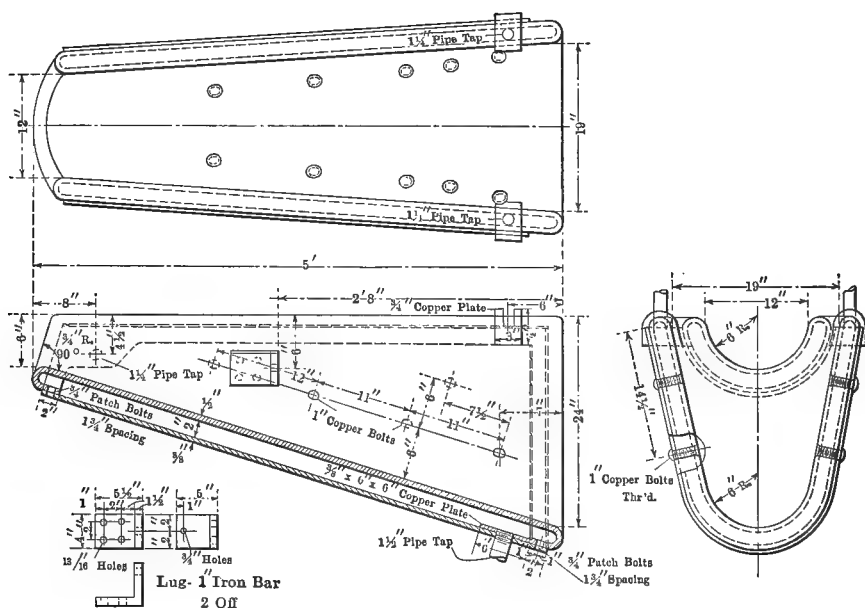
Glenn, *Tr. A. I. M. E.*, 1901, XXXI, 374.

<sup>6</sup> Poupin, *Eng. Min. J.*, 1912, XCIV, 785.

<sup>7</sup> Church, *Tr. A. I. M. E.*, 1913, XLVI, 436.



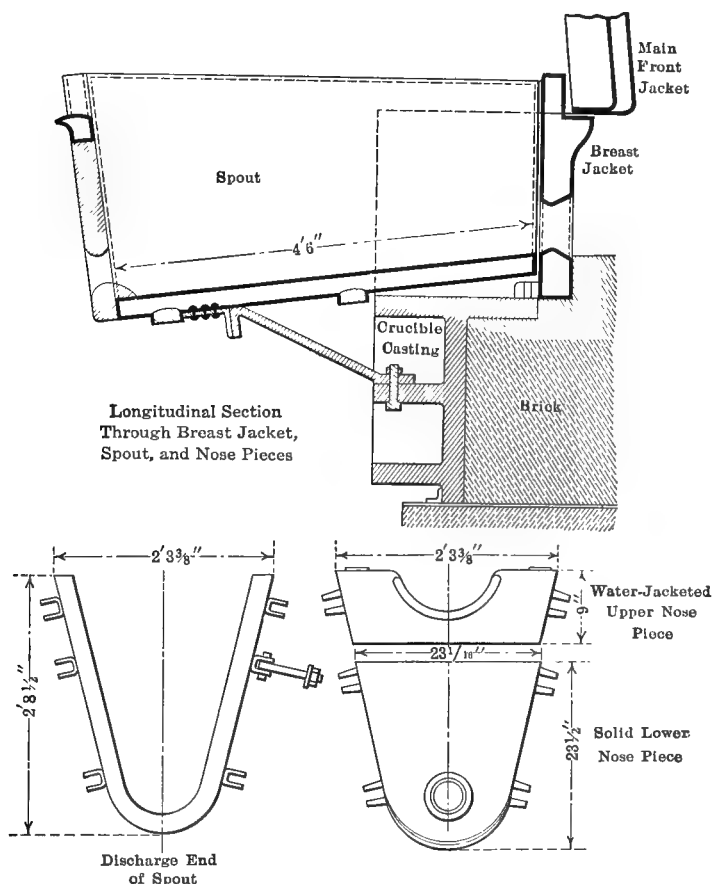
FIGS. 177-179.—Cast-iron tymp of Cananea blast-furnace.



FIGS. 180-182.—Wrought-iron water-cooled spout of Cananea blast furnace.

spouts. Each crucible has a tap-hole to empty the furnace. The latest furnace, 56×1044 in., has three continuous discharges.

Many materials have been tried in the construction of the water-cooled tymp and discharge-spout. The tymp is made usually either of cast-iron or of copper,<sup>1</sup> sometimes of fire-clay,<sup>2</sup> which requires frequent renewal. The cast-iron tymp of the Cananea furnace is shown in Figs. 177-179; the copper tymp of the Great Falls furnace in Figs. 165-167.



FIGS. 183-185.—New blast-furnace-spout of Great Falls.

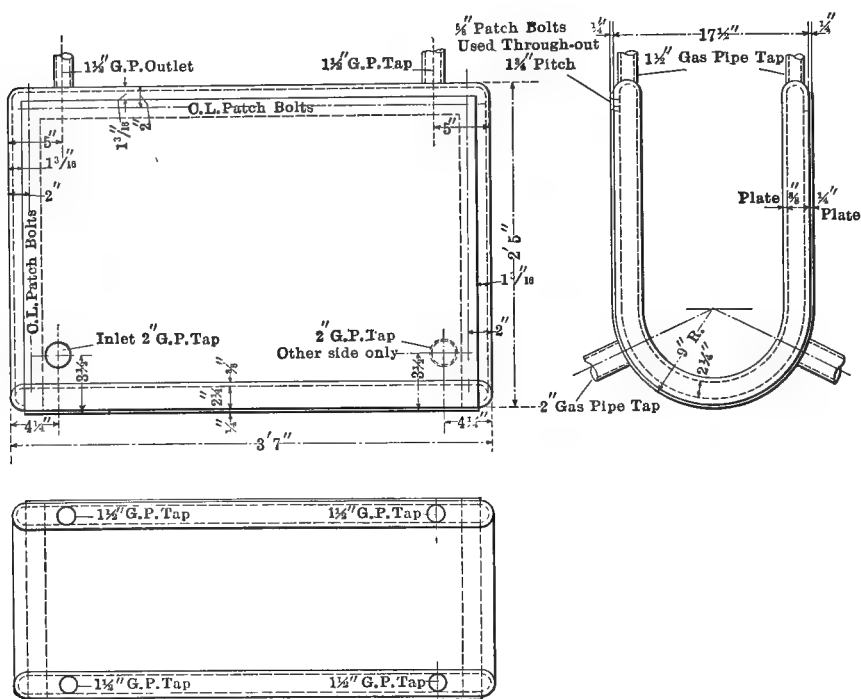
A spout<sup>3</sup> of solid cast-iron with water-cooled nozzle used to be common; wrought-iron pipe surrounded by cast-iron has proved unsatisfactory; a water-cooled wrought-iron spout, as the one at Cananea, shown in Figs. 180-182, especially if provided with a cast-copper removable nozzle, lasts a long time.

<sup>1</sup> Hixon, *Eng. Min. J.*, 1904, LXXVIII, 992.

<sup>2</sup> United Verde Copper Co., Vail, *Eng. Min. J.*, 1913, XCVI, 341.

<sup>3</sup> Hixon, *Eng. Min. J.*, 1905, LXXX, 673.

The spout, which usually rests with the lower end upon the breast-opening and with the upper upon the fore-hearth, is fastened by tie-rods to the breast-jacket. Ordinarily the floor of the crucible lies below the breast-opening and forms a well, which necessitates the tap-holes, mentioned above, to empty the crucible. At Great Falls,<sup>1</sup> the breast-opening is now placed at the lowest point of the crucible, and the trough of the spout, shown in Figs. 183-185, pitches downward from the breast-opening instead of inclining upward; thus the contents of the



FIGS. 186-188.—Blast furnace-spout of Copper Queen smelter.

crucible drain into the spout which has a tap-hole opposite the breast permitting the tapping the fluid contents of the furnace into the fore-hearth.

At the Copper Queen blast-furnaces the bottom of the crucible is flush with the breast-opening, and the wrought-iron water-cooled spout, shown in Figs. 186-188, with the bottom parallel to the sides is placed horizontally. A dam of refractory material, which has to be frequently patched or replaced, is rammed in the spout to trap the blast. If the furnace contents are to be drained, the dam is removed.

In some cases, especially with corrosive Ni-Cu matte, it has been found necessary to discard metal altogether and substitute for it magnesite or chrome

<sup>1</sup> Church, *Tr. A. I. M. E.*, 1913, XLVI, 436.

brick.<sup>1</sup> Such a spout is shown in Fig. 189, in which *A* is magnesite or chrome brick, *B* water-cooled copper nozzle, *C* cast-iron plate, *D* water-cooled tymp. At the works of the Canadian Copper Co., Copper Cliff, Ont., even the brick have had to be cooled by a water-coil placed next to casting *C*.

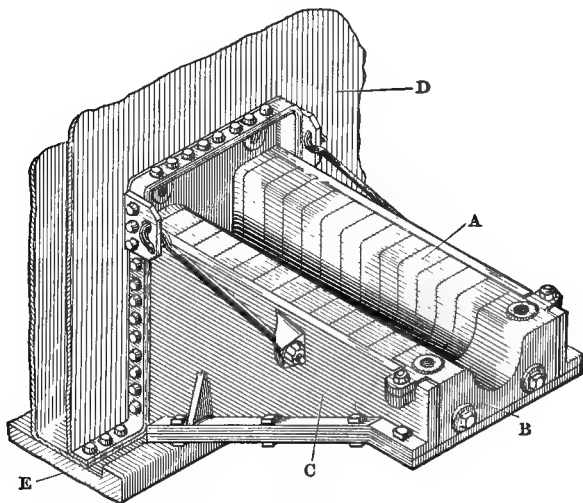


FIG. 189.—Blast-furnace-spout lined with magnesite- or chrome-brick.

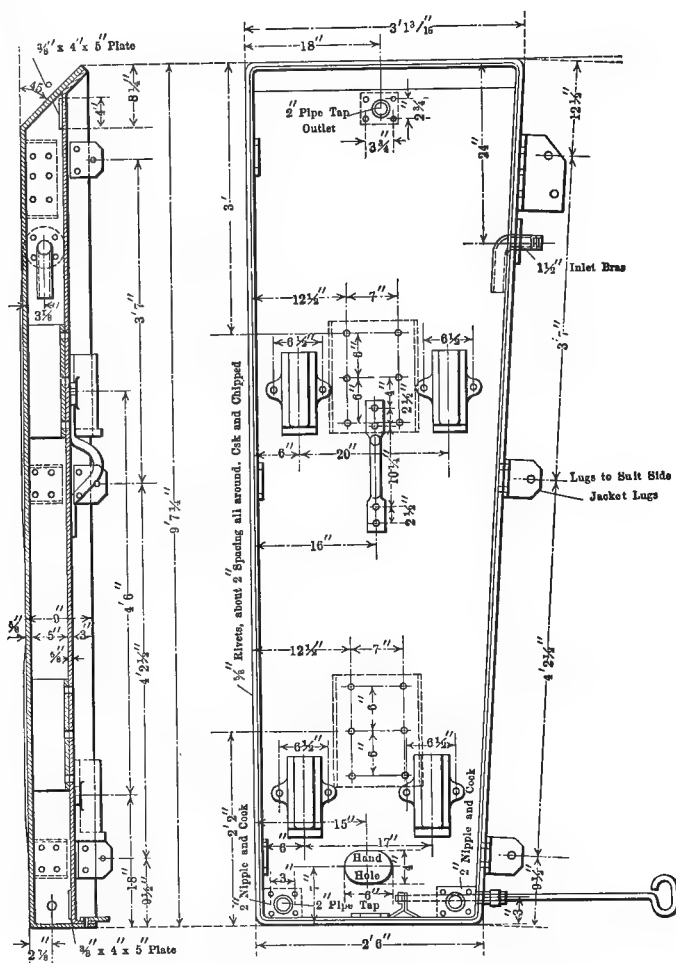
**92. The Shaft.**—The width of the oblong shaft at the tuyère-level shows a range of from 42 to 56 in., the length from 150 to 612 and even 1044 in. with the latest Mathewson furnaces at Anaconda. The advantages of increasing the length of a furnace are, saving of end-jackets, diminution of loss of heat by radiation and hence saving of fuel, and increase of regularity in operation and of smelting power. The investigations of Roberts<sup>2</sup> at Great Falls give numerical data for the fact that the saving in radiating surface by lengthening a furnace and thereby diminishing for a given area the surface occupied by the end-jackets, takes place at a rate which decreases as the furnace grows in length. The corollary is that the heat units carried away by the cooling-water of the jackets decrease at the same rate. This is the reason why Great Falls has adhered to 15 ft. as a standard length of the tuyère-section. However, at Anaconda, with a length of 87 ft., the saving in fuel has been from 10 to 15 per cent.; in addition there has been a reduction of floor area of 50 per cent., and of labor of 25 per cent. The tendency today is toward long furnaces.

The increase in area from tuyère to throat of furnace 1 : 1.30–1.60, is accomplished either by a bosh or by gradual enlargement. The Great Falls, Figs. 165–167, and Anaconda, Figs. 168–170, furnaces have a bosh of 1 in. per ft. for a distance of 7 ft. 5 in.; the rest of the shaft is vertical. The Cananea, Figs. 171–174, and most other furnaces show a gradual enlargement. The Mount

<sup>1</sup> Reeder, *Mines and Minerals*, 1911–12, XXXII, 55.

<sup>2</sup> *Tr. A. I. M. E.*, 1913, XLVI, 445.

Lyell furnace, Figs. 175-176, has vertical sides for a distance of 18 in., followed by a bosh 48 in. high with a total deflection of 4.5 in.; the rest of the shaft is vertical. The arrangement at Granby, B. C.,<sup>1</sup> is similar. At Keswick, Cal.,<sup>2</sup> cast-iron lower jackets similar to the Mount Lyell, and steel upper jackets were used.



FIGS. 190-191.—Cananea steel water-jackets, end.

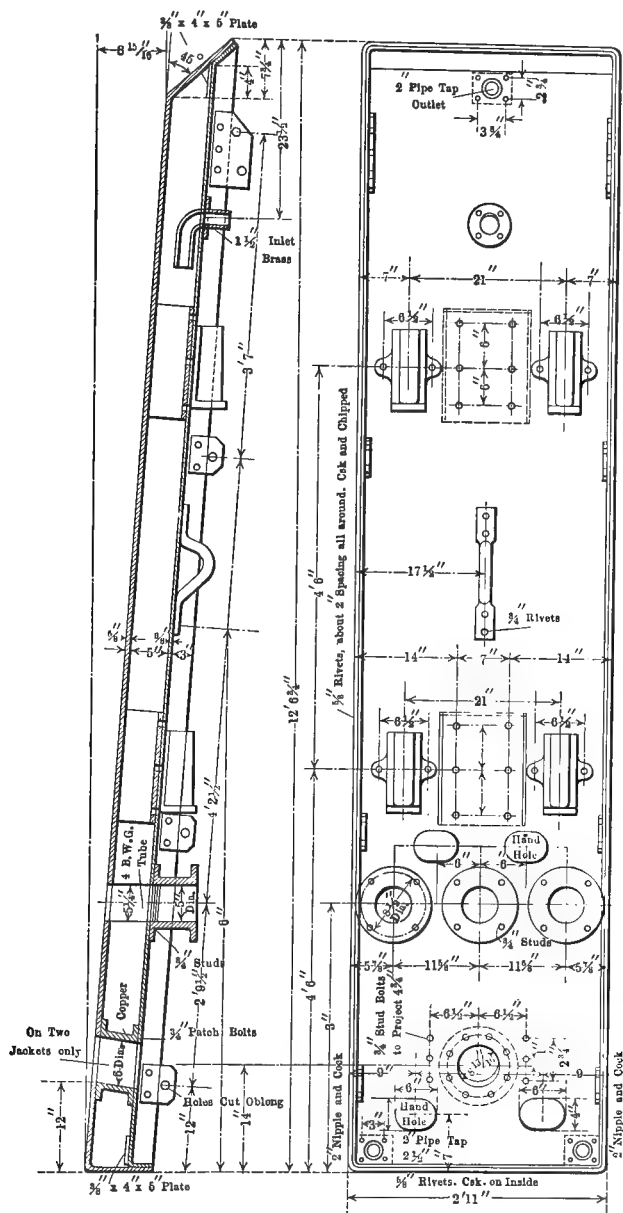
The working-height or smelting column is usually from 10 to 14 ft.; the level of the top of the charge is adapted to the coarseness of the mixture. Usually the sides of the furnace are built of two tiers of fire-box steel-plate jackets. The upper jackets either rest directly upon the lower, Figs. 165-167, or they are suspended by hangers from I-beams (mantle-frame) which carry the

<sup>1</sup> Lathe, *J. Can. Min. Inst.*, 1910, XIII.

<sup>2</sup> Keller, *Min. Ind.*, 1897, VI, 232.



structure above the feed-floor, Figs. 171-174. Upper and lower jackets are sometimes separated by a course of brick. The jackets are braced by longi-

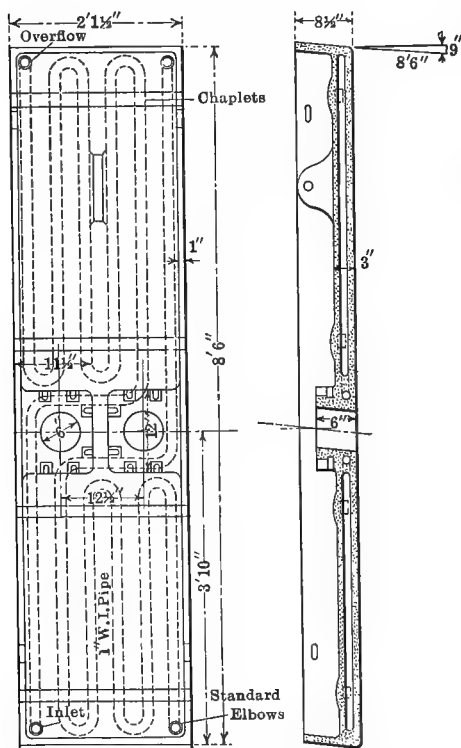


FIGS. 192-193.—Cananea steel water-jackets, side.

tudinal I-beams bound by tie-rods. The space between the tops of the upper jackets and the feed-floor is usually covered by cast-iron mantle-plates which

receive the impact of the charges as they are fed into the furnace. The water-jackets<sup>1</sup> are now nearly always flanged steel plates. The inner or fire-plate is made heavy,  $\frac{1}{2}$ – $\frac{7}{8}$  in. thick, to prevent buckling or warping,<sup>2</sup> the outer  $\frac{3}{8}$  in. thick; the former receives its support by distance-pieces, riveted to the outside plate, and offers a smooth strong surface to the descending charge. Stay-bolts on the inside plate, which used to burn off or be knocked off in barring or be attacked

by corrosive material settling at the junctions of bolts and jacket, especially along the tops of the upper row, have become almost obsolete. The flanges of the inner and outer plates are joined usually by riveting, sometimes by welding. The inner plate of a jacket appears to become more quickly



FIGS. 194-195.—Canadian Copper Company cast-iron water-jacket.

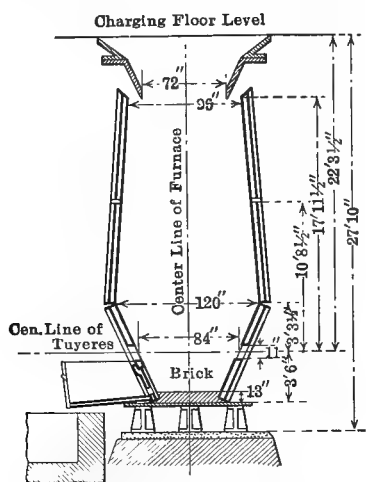


FIG. 196.—Wheeler 84 by 180 in. blast-furnace erected in 1911 at Great Falls.

corroded than the outer.<sup>3</sup> Many reasons and remedies have been suggested for the peculiar phenomenon.

Elevations and cross-sections of the single side- and end-jackets, 12 ft.  $6\frac{3}{4}$  in. and 9 ft.  $7\frac{1}{4}$  in. long, of the Cananea furnace are shown in Figs. 190-193.

At the smelter of the Canadian Copper Co.,<sup>4</sup> considerable trouble was experienced with the lower tier of steel jackets, holes being burnt into them by the strongly corrosive action of the matte. They were replaced in 1908 by

<sup>1</sup> *Eng. Min. J.*, 1904, LXXVII, 595 (Wethey); 797 (Lloyd); 1908, LXXV, 844 (Shelby); 1911, XCI, 653 (Rice); 1913, XCV, 612 (Holthoff).

<sup>2</sup> Rice, "Straightening of Warped Jackets," *Eng. Min. J.*, 1911, XCI, 653.

<sup>3</sup> Lee, *Tr. A. I. M. E.*, 1907, XXXVIII, 877; Discussion, 878, and 1908, XXXIX, 806.

<sup>4</sup> Reeder, *Mines and Minerals*, 1911-12, XXXII, 55.

thin cast-iron jackets enclosing water-cooled wrought-iron pipe-coils as shown in Figs. 194-195. They resist the action of the matte and last as long as nine months. When failure does take place, it is by cracking along a weak spot. The pipes are blown out from time to time with compressed air to remove any sediment that may have been deposited by the cooling-water.

The tuyère-stock in common use consists of a cast-iron tuyère-box, Figs. 165-167, firmly attached to the jacket and connected by a sheet-iron pipe, having a gate-valve,<sup>1</sup> with the bustle-pipe.

On page 148 it has been stated that the side-walls of all blast-furnaces either have a slight bosh or none at all, the walls being slightly inclined outward from tuyères to throat. A radical departure from this general type has recently been made by Wheeler at Great Falls,<sup>2</sup> who gave the furnace, as seen in Fig. 196, a vertical section similar to that of the iron blast-furnace, and in addition chose oblong vertical tuyère-openings instead of the circular in order to increase the area for the admission of air. The lower steel jackets, lined with a course of brick, rest on cast-iron plates supported by short cast-iron columns; there are 56 tuyères, and the slots are 11 by 3 in. The blast, 17,000-20,000 cu. ft. air per minute, is supplied by a turbo-blower<sup>3</sup> equipped with constant-volume governor. The blast is evenly distributed through the charge although the distance between tuyères is 84 in., no central core of unmelted charge has been observed. Some record runs show a smelting power per day of 7 tons of charge per square foot hearth area, accompanied by a saving of fuel over the usual furnace, 56 in. X 15 ft., which has a smelting power of 5.70 tons.

**93. Feeding of Charge and Withdrawal of Gases.**—Furnaces treating as much as 150 or even 200 tons of charge in 24 hr. may be fed by hand; usually furnaces with such a tonnage are fed by mechanical means, although some furnacemen<sup>4</sup> adhere to hand-feeding with a smelting capacity of 350 tons. The distribution of coarse and fine components of the charge between side and center, though probably not so well regulated in mechanical as in hand-feeding, is sufficiently to give a filling through which the gases will ascend in the manner desired. Four methods of mechanical feeding may serve as examples.

At the Great Falls<sup>5</sup> and Anaconda works,<sup>6</sup> a charge-train is brought by electric or compressed-air traction in flat side-tip cars alternately to one side and the other of the furnace, the doors are raised by compressed air, the cars are tilted by the same means, and the charges slid in. The coke is brought in two-wheel barrows of 30 cu. ft. capacity holding 900 lb. coke, and emptied into the furnace. By drawing from the bins into a charging-car first the fine and then the coarse ore, the latter will be projected toward the center of the furnace while the fine, gliding, will fall nearer the side. Varying the distance of top of

<sup>1</sup> Shelby, "Details of Cananea tuyère-valve," *Eng. Min. J.*, 1908, LXXXV, 848.

<sup>2</sup> Church, *Tr. A. I. M. E.*, 1913, XLVI, 437.

<sup>3</sup> Rosenblatt, *Min. Sc. Press*, 1913, CVI, 547.

<sup>4</sup> Johnson, *Eng. Min. J.*, 1902, LXXII, 251.

<sup>5</sup> Hofman, *Tr. A. I. M. E.*, 1904, XXXIV 289.

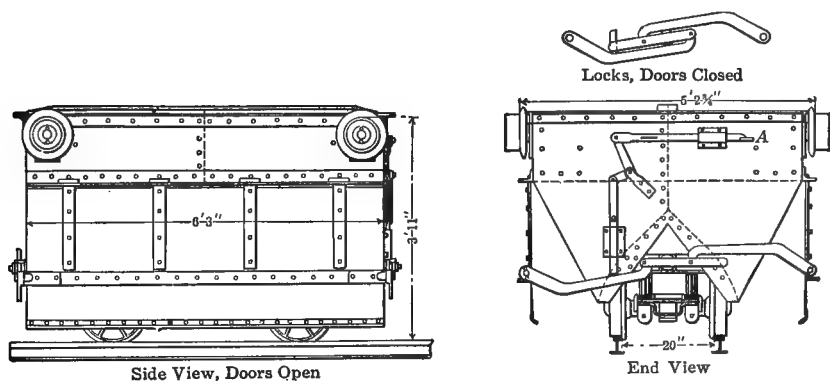
<sup>6</sup> Austin, *op. cit.*, 1906, XXXVII, 447, ill.



from the bedding floor (§ 177), is delivered at the top of the building by a 20-in. belt conveyor and discharged by an automatic tripper into the 75-ton storage-bin from which the material is withdrawn as needed into five 1-ton hoppers placed along one side of the furnace and closed by arc-gates. The chutes from the hoppers permit delivering the ore mixture either into the furnace over a sloping cast-iron plate or on to the feed floor. The bulk of the charge is run in direct, a small part is shoveled in for correcting irregularities and keeping the surface properly trimmed. The new furnaces at Teziutlan<sup>1</sup> have a similar feed.

At Mount Lyell, Figs. 175-176, the charges are dumped on the cast-iron plates in front of the feed-doors, and then pushed in mechanically.

With side-fed furnaces, the feed-opening usually occupies the entire length of the furnace; it is closed by a single (Cananea), by two (Great Falls) or more (Anaconda) balanced sheet-iron doors raised by compressed-air cylinders.



FIGS. 199-200.—Charging car of Granby smelter.

Often there is an additional door at either end (Great Falls, Anaconda). With the end-fed furnace, as at Granby, there are narrow side doors to furnish access for barring down and other purposes.

The gases are usually withdrawn from the furnace by means of a goose-neck leading into a dust chamber or a sheet-iron balloon-shaped flue. The structure carrying the downcomer used to be exclusively of brickwork; in some instances it has been made of sheet-iron, air-cooled and even water-cooled in order to prevent hot particles of flue-dust from combining with hot brickwork and forming heavy incrustations; any thin crusts formed on iron easily flake off. The Great Falls and Anaconda furnaces have brick superstructures; the Cananea, sheet-iron air-cooled; the Mammoth,<sup>2</sup> sheet-iron water-cooled. Fig. 201 represents a part end elevation and section of the closed top of No. 4 blast-furnace of the Tennessee Copper Co., Copper Hill, Tenn.,<sup>3</sup> which has been adopted as standard after trials of other forms. The gases from these furnaces

<sup>1</sup> Robinson, *Eng. Min. J.*, 1910, LXXXVIII, 655.

<sup>2</sup> *Min. Sc. Press*, 1908, XCVI, 30; *Min. World*, 1908, XXIX, 309; 1909, XXXI, 311.

<sup>3</sup> Emmons, *Tr. A. I. M. E.*, 1910, XLI, 723.

are utilized in the manufacture of  $\text{H}_2\text{SO}_4$ ,<sup>1</sup> hence the tops have to be closed. In the figure, longitudinal 24-in. I-beams, *a*, carry cast-iron corner-posts, *b*, as well as two dividers, *c*, making three divisions. The corner-posts carry 20-in. I-beams, *d*, which support the half-circle top, *e*, made of  $\frac{1}{2}$ -in. boiler plate and lined with 1.5-in. magnesia blocks followed by fire-brick. From the dome passes upward a vertical flue, *f*, 9 ft. in diameter inside the fire-brick lining, which

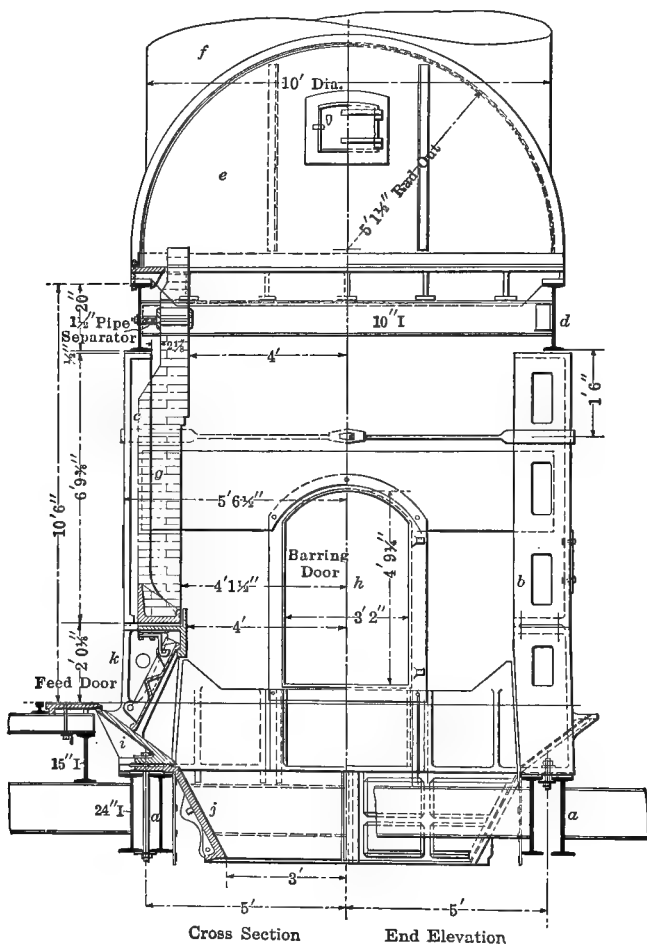


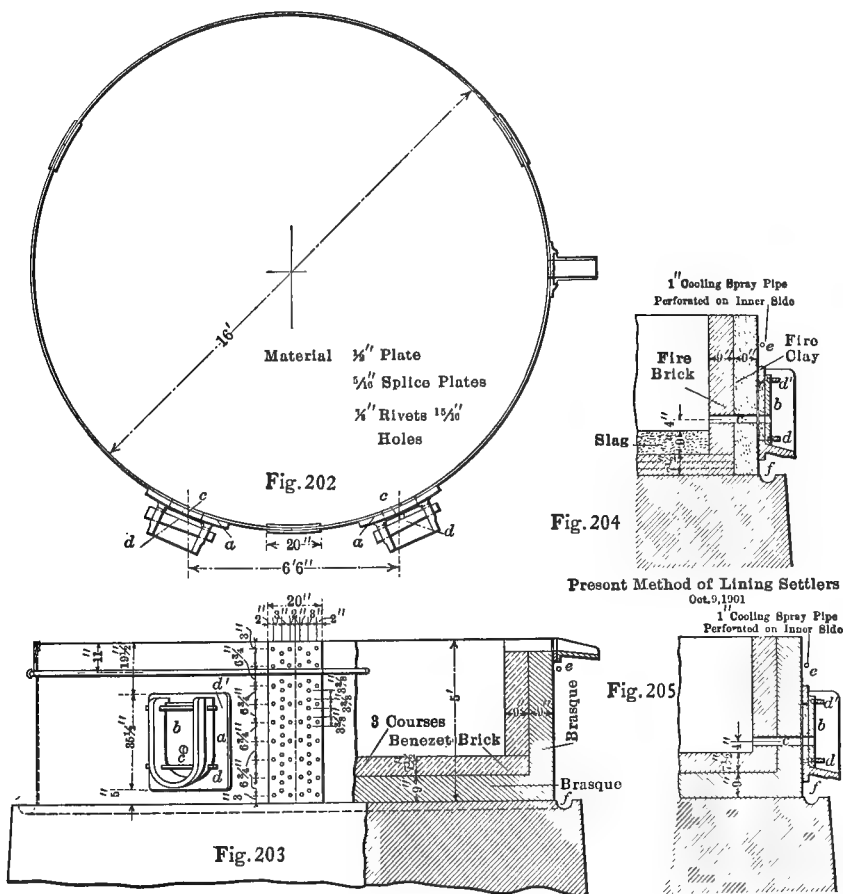
FIG. 201.—Closed top of blast-furnace, Tennessee Copper Co.

carries the sulphurous gases with 4.8–5.5 per cent. vol.  $\text{SO}_2$  to a dust chamber, for precipitation of dust and equalization of temperature, which they leave with a temperature of  $650^\circ \text{C}$ . to enter the Glover towers of the acid plant. The space between the corner-posts, *b*, is filled with a 13-in. wall, *g*, of fire-brick. At either end is a barring-door, *h*, of cast-iron lined with fire-brick. The 24-in.

<sup>1</sup> *Min. Res.*, U. S. Geol. Surv., 1911, II, 958.

I-beams, *a*, carry also the receiving- and apron-plates, *i* and *j*, for the charges. The feed-doors, *k*, three to a side, are of cast-iron; they are suspended, open inward, and are operated by a two-throw weighted switch-stand. They are gas-tight, and readily adjusted and easily repaired.

**94. The Fore-hearth or Settlers.**—In a modern large-size blast-furnace plant the matte produced usually goes direct to the converter; hence the fore-hearth



FIGS. 202-205.—Stationary settler, Great Falls, Mont.

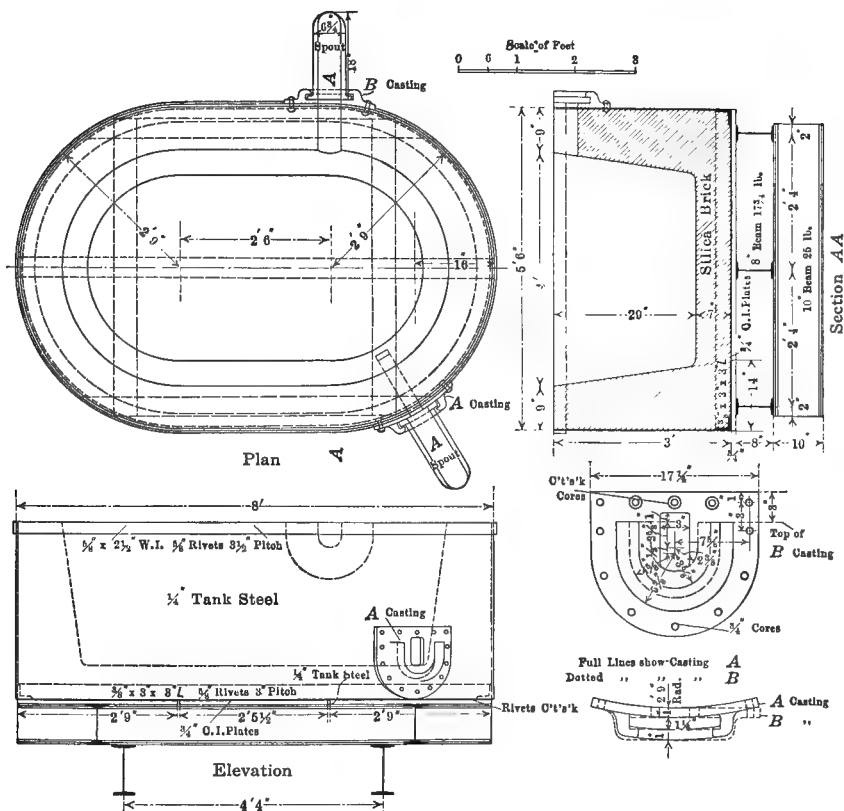
serves not only as a separator of matte from slag, but also a holder of matte from which as many as 10 tons are tapped at intervals into ladles and conveyed to the converting department. Direct-matte plants therefore have large settlers, while smelteries producing matte that is to be tapped into molds and allowed to solidify, are better served by medium-size or even small settlers.

A large settler is a fixed circular or oval boiler-iron shell, lined with refractory material, which usually has one slag-overflow and two matte-taps. The Great Falls circular fore-hearth, Figs. 202-205, is 16 ft. in diameter and 5 ft. deep; it





part-elevations in Figs. 206–208. Instead of the single rigid steel shell as at Great Falls, one-half of the shell is removable in three sections, two of which contain the matte-taps. This permits taking out a section and repairing it without disturbing the rest of the lining. The three removable tank-steel sections are 8 ft.  $2\frac{5}{8}$  in. long,  $\frac{1}{2}$  in. thick, and 5 ft. high; each overlaps its neighbor; two adjoining sections have lugs through which pass six  $2\frac{1}{4}$ -in. bolts 28 in. long; the space between two overlapping sections and the six bolts is filled by two



FIGS. 209–213.—Stationary settler, Butte Reduction Works.

plates,  $\frac{1}{2}$  and  $\frac{5}{8}$  in. thick, riveted together, thus preventing any bulging out of the steel owing to the expansion of the lining.

The settler is lined with a siliceous ore mixture of the same character as that used for the acid converters, and is rammed in a similar manner. This material stands better than did the brick formerly used, and has the further advantage that it costs nothing because it would have to be smelted in any case.

The bottom of the circular fore-hearth at Anaconda, 16 ft. in diameter, 5 ft. high, and of  $\frac{1}{2}$ -in. steel, is paved with silica brick,  $12 \times 6 \times 3$  in., set on end,

and then covered with a layer of crushed quartzite; the shell is lined with 15 in. of silica brick backed by 4 in. of crushed quartzite.

The bottom of the oval fore-hearth of Cananea, 22 ft. 6 in. long by 14 ft. wide by 4 ft. deep, and of  $\frac{3}{4}$ -in. steel, is lined with 10 in. of fire-brick,  $2\frac{1}{2}$  in. of which are replaced by chrome brick underneath the spouts and around the tap-holes; the sides are lined with 9 in. of chrome brick backed by 12 in. of ganister. On top of the side-lining is built a wall of clay,  $21\frac{3}{4}$  in. wide and 16 in. high, which increases the height of the settler from 4 ft. to 5 ft. 4 in.

A chrome brick<sup>1</sup> which has given much satisfaction in settlers has the following composition:  $\text{SiO}_2$  3,  $\text{Al}_2\text{O}_3$  24,  $\text{Fe}_2\text{O}_3$  16,  $\text{MgO}$  14,  $\text{Cr}_2\text{O}_3$  40.

In Figs. 209-213 is represented the small stationary oval settler, 8 by 7 by 3 ft., of the Butte Reduction Works, lined with fire-brick without any backing;

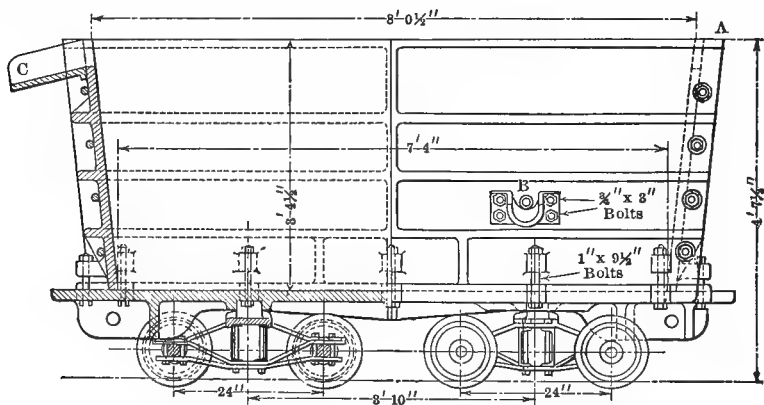


FIG. 214.—Movable oblong settler or fore-hearth.

it serves a blast-furnace, 42 by 112 in. at the tuyère-section, which treats in 24 hr. 125 tons of charge. The matte is tapped at intervals into molds, broken, and shipped.

The drawings of fore-hearths show that the matte-tap is an oval slot backed by a block, which is either cast-iron or preferably copper, and contains the tap-hole. Hixon<sup>2</sup> recommends for the cutting 40 per cent. Ni-Cu matte a carbon block, made of electric-light carbon, 5 in. thick with a 2-in. bore, protected by a cast-iron plate.

The tap-hole is stoppered with a clay plug pushed in firmly with the rod (dolly) and driven home by a few gentle strokes of a hammer. In order to facilitate the tapping later on, the tapping-bar is driven through the soft clay plug until it reaches the hardened interior. It remains in this position until the next tap.

A movable fore-hearth, 8 ft.  $\frac{1}{2}$  in. by 4 ft.  $1\frac{1}{2}$  in. by 3 ft.  $4\frac{1}{2}$  in., constructed of heavy ribbed cast-iron plates held together by threaded rods and nuts and lined

<sup>1</sup> Editor, *Eng. Min. J.*, 1912, xciv, 689.

<sup>2</sup> *Op. cit.*, 1905, LXXX, 673.

with fire-brick, is shown in Figs. 214–215; *A* is the slag-matte inlet, *B* the matte-tap, and *C* the slag-outlet. Sometimes several fore-hearths of this type are placed in series as, *e.g.*, at the Mount Lyell works, Figs. 175–176, three fore-hearths, 6 ft. long by 4 or 5 ft. and  $3\frac{1}{2}$  ft. high lined with 9 or 12 in. of fire-brick.

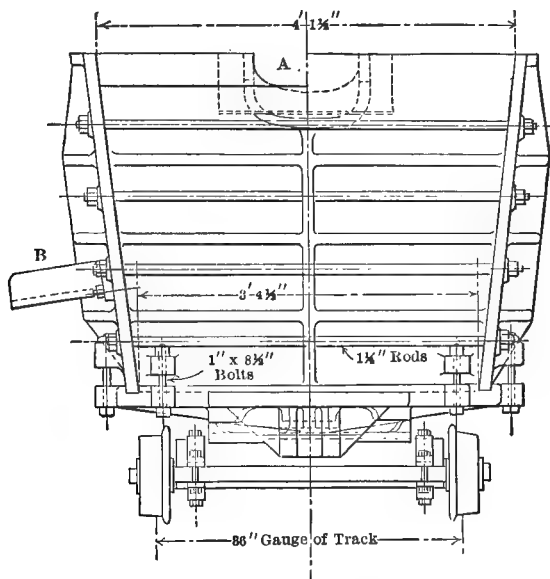


FIG. 215.—Movable oblong settler or fore-hearth.

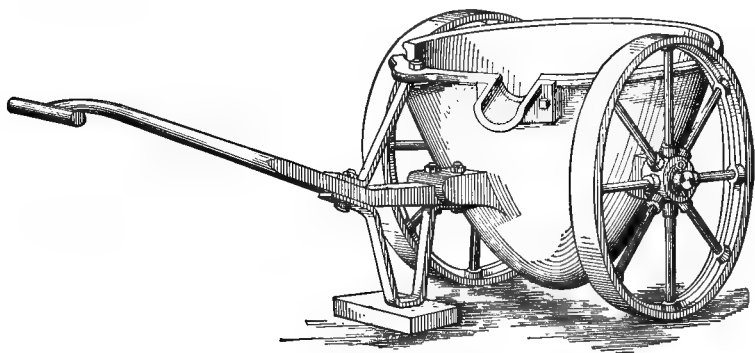


FIG. 216.—Overflow slag-pot.

The smallest form of fore-hearth is represented by an overflow slag-pot shown in Figs. 216–217. It usually serves to collect particles of matte which have not settled in the larger fore-hearth on account of the stirring-up caused by the steady inflow of slag-matte.

**95. Disposal of Waste-slag.**—The waste-slag is disposed of either by collecting in pots which are hauled singly or in trains to the dump by animal, steam,

compressed-air, or mostly electric power,<sup>1</sup> and poured; or the slag is granulated by a jet of water under suitable head impinging upon it, and then carrying it either to the dump or into a river.<sup>2</sup> The slag-cars vary in size and construction. Fig. 218 represents a car of the Traylor Engineering Co. made in sizes to hold from 5 to 15 tons. The bowl, of cast steel, is made in two sections. Frequently

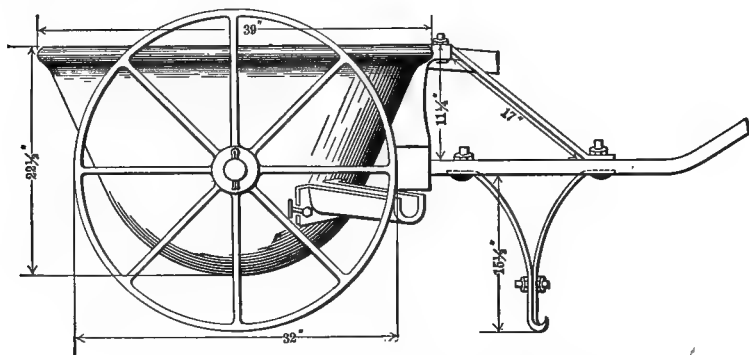


FIG. 217.—Overflow slag-pot with matte-tap.

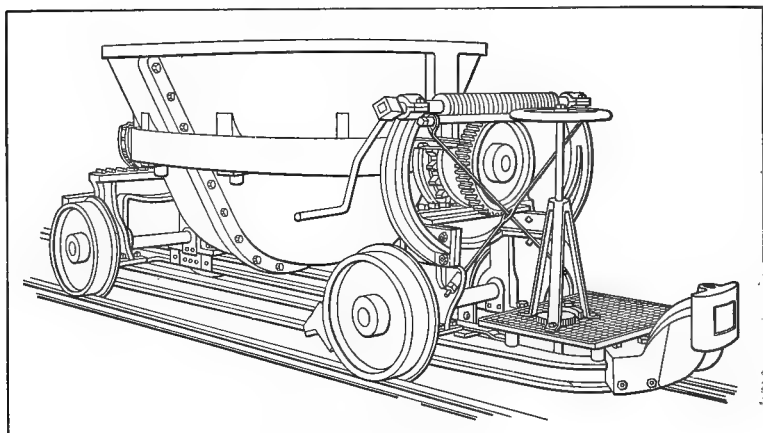


FIG. 218.—Waste-slag car.

there are five sections,<sup>3</sup> the bottom and four side sections, all flanged and bolted together. The bowl is supported by a steel ring riveted to pinion-toothed trunnions which roll on a rack-track. In Fig. 218, the bowl is dumped by a worm gear;<sup>4</sup> with small bowls dumping by lever is not uncommon; large bowls

<sup>1</sup> Slag-car of Tooele, Utah, *Eng. Min. J.*, 1913, xcv, 617.

<sup>2</sup> Hixon, "Granulation of Slag at Mond Nickel Works, Ontario," *Eng. Min. J.*, 1906, LXXXII, 553.

Bergwith, Granulating Process, " *Eng. Min. J.*, 1913, xcvi, 55.

<sup>3</sup> Reeder, *Mines and Minerals*, 1910, XXXI, 149.

<sup>4</sup> Slag-car of Tooele, Utah, *Eng. Min. J.*, 1913, xcv, 617.

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are frequently tilted electrically or by means of compressed air or by a spring lever.<sup>1</sup>

The Jones-Bennetts pot<sup>2</sup> of the Tacoma Smelting Co. has a scoop-shaped bowl.

At Greenwood, B. C.,<sup>3</sup> an auxiliary tilting slag-bowl, 4-5 ft. in diameter and 2 ft. deep, is swung under the slag-spout of the settler during the period of changing the Pollock slag-pots,<sup>4</sup> and thus spilling of slag avoided.

Cast-iron slag-pots, similar to the one shown in vertical section in Fig. 219, serve the purpose of collecting about 500 lb. of slag.<sup>5</sup>

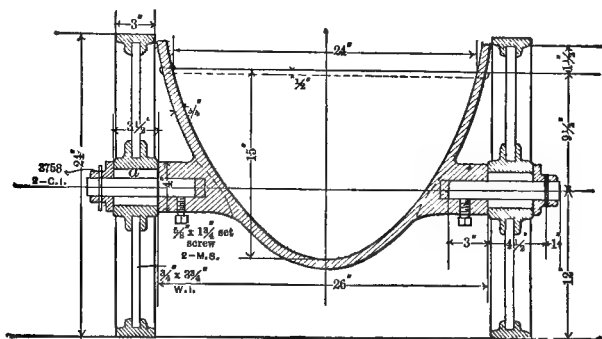


FIG. 219.—Waste-slag pot.

Slag-casting machines, such as the Bennetts,<sup>6</sup> at the Tacoma blast-furnaces, are exceptional with blast-furnaces, but not uncommon with converters.

**96. Disposal of Matte.**—The matte is collected from the fore-hearth in ladles made of heavy steel plate or cast steel stiffened to withstand the strains; spout and trunnions are of cast steel. Single-trunnion ladles are made in sizes to hold from 5 to 10 tons of matte; they are either suspended from an overhead traveling crane or supported by a car as is a slag-bowl. The Shelby double-trunnion ladle, represented in Figs. 220-223, is used at Cananea and Cerro de Pasco; it has over the single-trunnion the advantage that it is always in balance whether full or empty.

In some cases a ladle is lined with ganister; generally, however, it is first used as a slag-ladle when the skull of adhering slag forms a protective coating.<sup>7</sup> If matte is to be allowed to solidify, it is tapped into sand or iron molds; special forms to facilitate handling have come into use, such as those of Rhodes,<sup>8</sup> Bennett,<sup>9</sup> Kilker.<sup>10</sup>

<sup>1</sup> Shelby, Slag-car of Cananea, *Eng. Min. J.*, 1909, LXXXVII, 204.

<sup>2</sup> Jones-Bennetts, *Tr. A. I. M. E.*, 1906, XXXVI, 223.

<sup>3</sup> Editor, *Eng. Min. J.*, 1910, LXXXIX, 904.  
McAllister, *op. cit.*, 1911, XCI, 1011.

<sup>4</sup> *Eng. Min. J.*, 1911, XCI, 660.

<sup>5</sup> Keller, *Tr. A. I. M. E.*, 1893, XXII, 575, 675 (Neill).

<sup>6</sup> Austin, *Min. Sc. Press*, 1907, XCIV, 282.

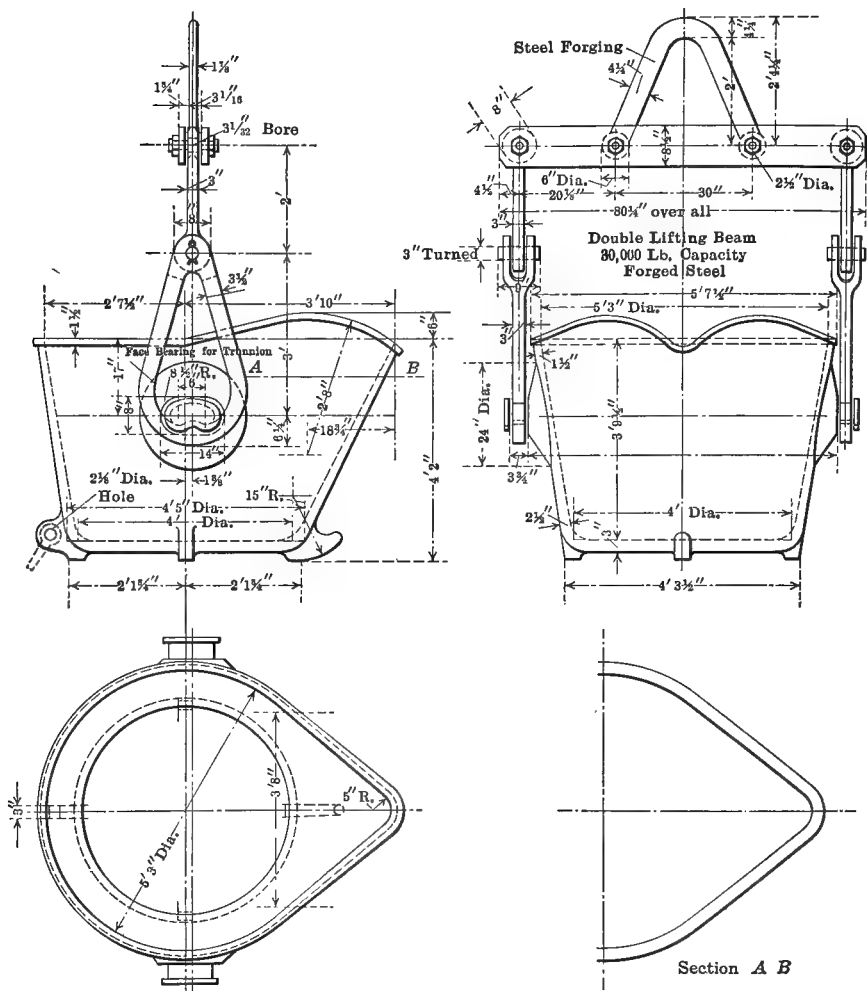
<sup>7</sup> "Matte-car and Conveyor, Mammoth Smelter," *Eng. Min. J.*, 1911, XCII, 675, 832, 932.

<sup>8</sup> Braden, *Tr. A. I. M. E.*, 1896, XXVI, 46.

<sup>9</sup> Bennett, *Eng. Min. J.*, 1908, LXXXV, 252.

<sup>10</sup> Havard, *Eng. Min. J.*, 1909, LXXVII, 1294.

**97. Blast-furnace Table.**<sup>1</sup>—In Table 28 are assembled the principal constructive features and working results of some of the leading blast-furnaces. Other facts are brought together in the selected literature.<sup>2</sup> The abstracts in



FIGS. 220-223.—Shelby double-trunnion matte-ladle.

<sup>1</sup> Additional Data: Borchers, *Metallurgie*, 1905, II, 419; 1907, IV, 104.  
Ralli, *Rev. Un. Min.*, 1911, XXXIV, 216.  
Peters, "Practice of Copper Smelting," 1911, p. 146.

## <sup>2</sup> REFERENCES TO BLAST-FURNACE PLANTS

- Balaklala Consolidated Copper Co.: Mauch, *Mines and Minerals*, 1908, XXVIII, 411;  
"Report," *Eng. Min. J.*, 1909, LXXXVII, 504; Martin, *Min. Sci.*, 1911, LXIII, 338.  
Blagodatny Smelter: Ortin-Lange, *Metall.-Erz.*, 1913, X, 543, 586, 612.  
Bogoslowsk Smelter: Davey, *Tr. Inst. Min. Met.*, 1913, XXII, 591; *Eng. Min. J.*, 1913, XCV, 605; *Min. Eng. World*, 1913, XXVIII, 711.



Mineral Industry by L. S. Austin give additional information. Some data about European furnaces, considered to be representative, have been added to table 28.

The furnaces in the United States and Canada are oblong and of large capacity. The width at the tuyères ranges from 44 to 56 in., and the length from 266 to 1044 in. The working height, distance from tuyères to throat, is given as ranging from 10 to 17 ft. This large diversity is only apparent, as in some cases the figures represent only the height of charge, and this usually is 10 or 12 ft., depending upon the coarseness of ore and flux; the finer the particles, the smaller the working height in order to obtain an open charge. The ratio of

- Boston and Montana Consol. Copper Min. Co.: Hofman, *Tr. A. I. M. E.*, 1904, XXXIV 284; Higgins, *Eng. Min. J.*, 1909, LXXXVII, 156.
- Britannia S. Co.: *Min. Ind.*, 1906, xv, 261.
- Bully Hill Smelter: Martin, *Min. Sci.*, 1908, LVIII, 345.
- Butte Red-works: Wethey, *Eng. Min. J.*, 1908, LXXXVIII, 1153.
- Canadian Copper Co.: Browne, *Can. Min. J.*, 1907, I, 305; *Eng. Min. J.*, 1908, LXXXV, 557; Turnbull, *Mines and Minerals*, 1910, XXXI, 121.
- Cananea Cons. Copper Co.; Ore-Bedding, Woodbridge, *Eng. Min. J.*, 1906, CXXXII, 624; Messiter, *Min. Sc. Press*, 1907, XCIV, 539, XCV, 528; Elsing, *Min. Sc. Press*, 1912, CIV, 619; "Blast-furnace," Shelby, *Eng. Min. J.*, 1908, LXXXV, 841, 867; "Dust," Shelby, *Eng. Min. J.*, 1908, LXXXV, 204; "Plant," Findlay, *Min. Sc. Press*, 1905, XCI, 360; Brinsmade, *Mines and Minerals*, 1907, XXVII, 264, 465; Herrick, *op. cit.*, 1909, XXX, 65; Reeder, *op. cit.*, 1911, XXXII, 55.
- Cerro de Pasco: Strauss, *Min. Sc. Press*, 1908, XCVII, 637; *Min. World*, 1910, XXXII, 709; Lloyd, *Tr. Met. Inst. Min. Met.*, 1909-10, I, 11.
- Copper Queen Cons. Min. Co.: Editor, *Eng. Min. J.*, 1905, LXXX, 197; Woodbridge, *op. cit.*, 1906, LXXXII, 242, 298 (blast-furnace, ore-bedding); Brinsmade, *Mines and Minerals*, 1907, XXVII, 273; Milton, *op. cit.*, 1909, XXX, 148; Lee, *Eng. Min. J.*, 1910, xc, 504 (Dust); Rose, *Glück Auf*, 1911, XLVII, 107.
- Douglas Smeltery: Barbour, *Eng. Min. J.*, 1908, LXXXV, 303; Tucker, *op. cit.*, LXXXVI, 413.
- Ducktown Sulphur, Copper & Iron Co.: Alabaster-Wintle, *Tr. Inst. Min. and Met.*, 1905-06, xv, 274; Freeland, *Eng. Min. J.*, 1903, LXXV, 664.
- Garfield Smeltery: Beason, *Eng. Min. J.*, 1906, LXXXI, 509; Ingalls, *op. cit.*, 1907, LXXXIV, 576; Brinsmade, *Mines and Minerals*, 1908, XXVIII, 305; Kroupa, *Oest. Jahrb.*, 1908, LVI, 213.
- Granby Cons. Min., Sm. & Power Co.: Hodges, *J. Can. Min. Inst.*, 1908, XI, 408; Sacket, *Mines and Minerals*, 1910, XXX, 524; Lathe, *J. Can. Min. Inst.*, 1910, XIII, 275; Jacobs, *Met. Chem. Eng.*, 1911, IX, 406; 1912, x, 113; Avery, *Eng. Min. J.*, 1912, XCIII, 935; Lee, *Met. Chem. Eng.*, 1912, x, 147.
- Great Cobar Smelting Works: Correspondent, *Eng. Min. J.*, 1908, LXXXV, 950; Austin, *Min. Ind.*, 1911, XX, 225.
- Greenwood Copper Smelting Works: McAllister, *Eng. Min. J.*, 1911, xci, 1011; Bell, *Tr. Can. Min. Inst.*, 1913, XVI, 152.
- General: Christensen, *Eng. Min. J.*, 1908, LXXXVI, 847; *Min. World*, 1909, XXX, 381; 1910, XXXIII, 489.
- Horseshoe Mg. Co.: Fulton-Knutzen, *Tr. A. I. M. E.*, 1905, XXXV, 326.
- International S. & R. Co.: Palmer, *Min. World*, 1910, XXXII, 419; *Mines and Minerals*, 1911, XXXI, 321; *Mines and Methods*, 1909-10, I, 149; Repath-McGregor, *Met. and Chem. Eng.*, 1911, IX, 15; Thomson-Sicka, *Tr. A. I. M. E.*, 1913, XLVI.
- Kyshtim Smelter: Carlyle, *Eng. Min. J.*, 1912, XCIII, 1231; Lange, *Metall-Erz.*, 1913, x, 108.
- Mammoth Copper Min. Co.: Campbell, *Min. Sc. Press*, 1908, xcvi, 30; Martin, *op. cit.*, 1908, XXIX, 309; 1909, XXXI, 311; *Min. World*, 1908, XXIX, 310; Haskell, *Mines and Methods*,

throat to hearth area is about as 1.3:1, showing that with a working height of about 12 ft. the sides are very steep, or that most furnaces aim to have very little reducing action in the shaft. This is shown similarly by the very small amount of bosh of the jackets. The water-jackets in nearly all cases extend down to the bottom of the crucible. Most of the tuyères are 4 and 5 in. in diameter; the tuyère-ratio shows a considerable variety, which seems to prove that there exists still a diversity of opinion upon this point; its explanation lies in part in the character of the ore treated.

### (a) REDUCING SMELTING

**98. Reducing Smelting in the Blast-furnace of Roasted (Raw) Sulphide Ore for Matte.**—A reducing fusion in the blast-furnace is a process in which enough carbonized fuel is added to the ore-charge to furnish the reduction and the heat necessary for the operation. It is intended that the blast shall oxidize only the C and no S. Any elimination of S as  $\text{SO}_2$  taking place during the descent of the charge in the furnace may be due to oxidation by the ascending gas current, but is probably caused by the action in the charge of oxide upon sulphide.

Roasted sulphide copper ore contains oxides, sulphates, and under/composed sulphides of Cu and Fe, subordinately also of Zn, Pb, Mn, perhaps some As and Sb-compounds, and the gangue. In the reducing fusion, Cu, Fe, and S form a matte which takes up the precious metals and part of the Zn, Pb, As,

1908, XXXVIII, 392; Rice, *Eng. Min. J.*, 1911, XCI, 614; Tupper, *Min. Eng. World*, 1912, XXXVI, 337.

Mason Valley Smelter: Read, *Min. Sc. Press*, 1912, cv, 267.

Mount Lyell Min. and Ry. Co.: Sticht, *Min. Ind.*, 1907, xvi, 428; *Metallurgie*, 1906, III, 563, 591, 638, 664, 686, 709, 760, 788 (drawing of blast-furnace, *Min. Ind.*, 1907, xvi, 350).

Rio Tinto, Baron, *Min. World*, 1909, XXXI, 681.

Shannon Copper Co.: Corresp. *Min. Sc. Press*, 1902, LXXXIV, 101.

Tennessee Copper Co.: Heywood, *Eng. Min. J.*, 1904, LXXVII, 231; Alabaster-Wintle, *Tr. Inst. Min. Met.*, 1905-06, xv, 269; Channing, *Eng. Min. J.*, 1905, LXXIX, 1195; LXXX, 6; *Min. Sc. Press*, 1908, xcvi, 97; Freeland-Renwick, *Eng. Min. J.*, 1910, LXXXIX, 116; Guess, *op. cit.*, 1910, xc, 866; Morgan, *Min. Sc. Press*, 1910, ci, 677; Falding-Channing, *Eng. Min. J.*, 1910, xc, 555; Emmons, *op. cit.*, 1911, xci, 15; *Tr. A. I. M. E.*, 1910, xli, 723; Nelson, *Mines and Methods*, 1912, III, 407; *Min. Sc.*, 1912, LXV, 149; Offerhaus, *Metall-Erz.*, 1913, x, 863.

Teziutlan Smeltery: Corresp. *Eng. Min. J.*, 1909, LXXXVIII, 655; 1910, xc, 169.

Trail Smeltery: Turnbull, *Mines and Minerals*, 1910, XXXI, 121; Buchanan, *Tr. Can. Min. Inst.*, 1913, xvi, 156.

Tyee Copper Co.: Maynard, *Eng. Min. J.*, 1909, LXXXVIII, 905; Jacobs, *op. cit.*, 1912; Phelps, *Min. Sc. Press*, 1907, xcv, 782; "B. C. Report Minister of Mines," 1902, 243.

United States Metals Refining Co.: Vail, *Eng. Min. J.*, 1913, xcv, 1031; xcvi, 553.

United Verde Copper Co.: Vail, *Eng. Min. J.*, 1913, xcvi, 287, 341.

Walleroo Smelter: Cloud, *Tr. Inst. Min. Met.*, 1906, xvi, 55, 100.

Washoe Plant: Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 258; Austin, *op. cit.*, 1906, XXXVII, 431; Corresp., *Mines and Minerals*, 1907, XXVIII, 131, 248; Offerhaus, *Eng. Min. J.*, 1908, LXXXV, 1189, 1234; LXXXVI, 747; 1909, LXXXVIII, 243.

Yampa Smeltery: Palmer, *Min. Sc. Press*, 1909, xcix, 225; Christensen, *Min. World*, 1909, XXX, 621.

and Sb; the gangue with the necessary fluxes form the slag, consisting of  $\text{SiO}_2$ ,  $\text{FeO}$  and  $\text{CaO}$ , some  $\text{Al}_2\text{O}_3$ <sup>1</sup> and other bases. The formation temperatures with the effects of different bases have been discussed elsewhere.<sup>2</sup> As it usually takes many tons of ore, or slag, to make 1 ton of matte, the ratio of concentration being  $10 \pm 1$ , the composition and character of the slag to be formed is one of the first considerations in making up the charge.

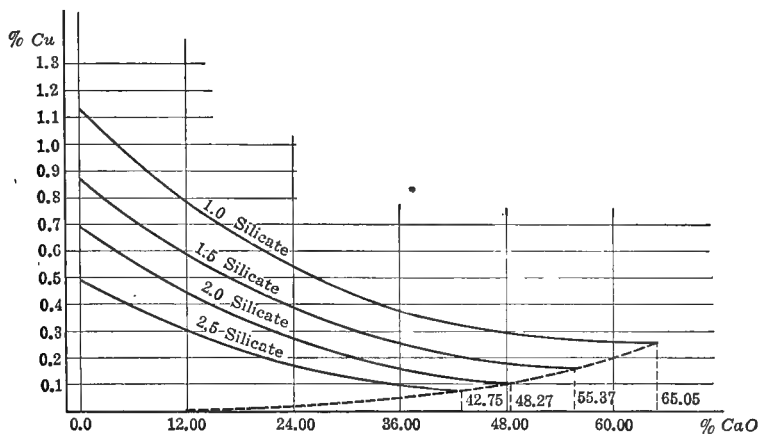


FIG. 224.—Solubility of  $\text{Cu}_2\text{S}$  (30-per cent. matte) in ferro-calcic silicates with increasing percentages of  $\text{CaO}$ .

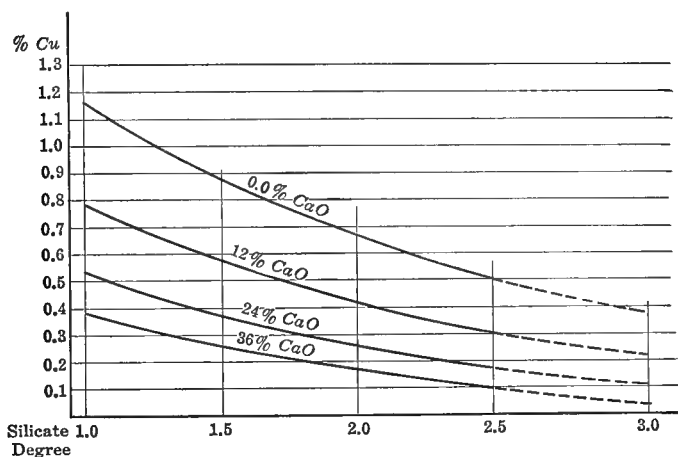


FIG. 225.—Solubility of  $\text{Cu}_2\text{S}$  (30-per cent. matte) in ferro-calcic silicates of different degrees of silication.

**99. Blast-furnace Slag in Reducing Smelting.**—The slags formed in the reducing smelting of roasted sulphide copper ore show a great variety in silicate-

<sup>1</sup> Bellinger, *Eng. Min. J.*, 1912, xciv, 321; *Min. Sc. Press*, 1912, cv, 114; *Met. Chem. Eng.*, 1912, x, 693.

<sup>2</sup> Hofman, "General Metallurgy," 1913, p. 454-463.

degree and composition. The former ranges from sub- to bi-silicate, but usually is near a singulo- and sesqui-silicate. With ores rich in Fe, the percentage of  $\text{SiO}_2$  covering a range of from 28 to 40 per cent.,  $\text{FeO}$  is generally high (50 per cent.) and  $\text{CaO}$  low (10 per cent.); the reverse is the case with ores containing little Fe;  $\text{Al}_2\text{O}_3$  is rarely high (15 per cent.), more frequently low (4 per cent.) than medium (8 per cent.). The main requirements that the slag has to fulfil<sup>1</sup> are that it shall form at a low temperature, require little superheating to be fluid, have a specific gravity not too high to allow a satisfactory settling and separation of matte, and be cheap, *i.e.*, not require much flux. There is little danger

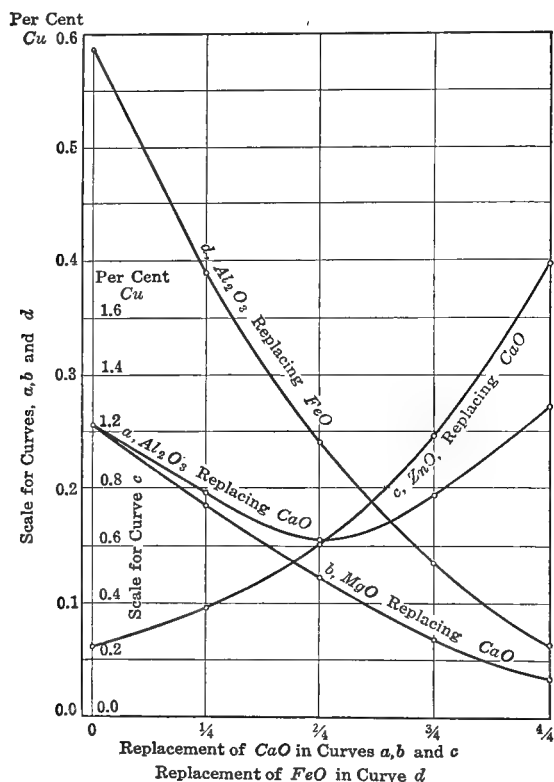


FIG. 226.—Effect of replacement of  $\text{FeO}$  and  $\text{CaO}$  by  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{ZnO}$  in a sesqui-ferro-calcic silicate upon the solubility of  $\text{Cu}_2\text{S}$  (30-per cent. matte).

of  $\text{Cu}$  being scorified as long as there is enough  $\text{FeS}$  present to sulphurize any metallic or silicate of copper that may have entered the furnace or have been formed in the downward passage of the charge.

Wanjukow<sup>2</sup> has investigated in the laboratory the solubility of  $\text{Cu}_2\text{S}$  of a 30-per cent. matte in ferro-calcic silicates. He finds that the solubility falls with the degree of silication as shown in Fig. 224; and that it decreases with the

<sup>1</sup> Mostowitsch, *Metallurgie*, 1912, IX, 559.

<sup>2</sup> *Op cit.*, 1912, IX, 1, 48.

replacement of FeO by CaO, Fig. 225. The results of the effects of replacement of the constituents FeO and CaO by the bases  $\text{Al}_2\text{O}_3$ , MgO and ZnO in two sesqui-silicate slags are assembled in Fig. 226. Here curves *a*, *b*, and *c* represent the solubility of  $\text{Cu}_2\text{S}$  (30-per cent. matte) in the sesqui-silicate  $\text{SiO}_2$  42.42, FeO 21.58, CaO 36.00; and curve *d*, that in the sesqui-silicate  $\text{SiO}_2$  39.78, FeO 48.22, CaO 12.00.

In general, slags which contain a metal having much affinity for S will carry more Cu than those which have little. In the following list by Wanjukow, Cu stands at the head, Al at the bottom: Cu, Ni, Co, Fe, Mn, Zn, Ca, Mg, Al.

The effects of varying percentages of Cu in matte upon the Cu-content of slags is taken up in § 119.

The compositions of slags formed in a reducing smelting may be the same as those made in pyritic smelting (§ 106) or in partial pyritic smelting (§ 110, 111) as the latter must fulfil requirements similar to the former as far as specific gravity and fluidity are concerned. On account of the great latitude in composition, and of the fact that smelteries usually treat ores from a single district, typical slags, such as have been developed in lead-smelting, have not been devised, although these will work in the reducing fusion of a copper blast-furnace as they do in that of the lead blast-furnace.

When the leading ore was a cupriferous pyrite or pyrrhotite with little gangue, the slags made consisted mainly of  $\text{SiO}_2$  and FeO, totaling over 90 per cent., the remainder being small amounts of  $\text{Al}_2\text{O}_3$  and earthy bases. The investigations of Hofman<sup>1</sup> have shown that with pure ferrous silicates the formation temperatures decrease as the silicate-degree rises, but experience has proved that the reverse is the case with fluidity; the singulo-silicate forms at a higher temperature and is more fluid than the bi-silicate, and the 3:4 or the 2:3 silicates lie between the two. The curves of Hofman also show that the replacements of FeO by CaO lower the formation temperatures to a certain point, beyond which they rise again; also that low- $\text{SiO}_2$  ferrous slags can endure more CaO before they reach the minimum than high- $\text{SiO}_2$  slags. Experience has shown that additions of CaO up to certain amounts increase the fluidity. These statements give the reasons for the preference of the 1:1 and 2:3 ferrous silicates over those that are either more basic or more acid. With slags more basic there is danger of hearth accretions, with slags more acid, there is either a small tonnage or a high coke-consumption to give the slags the required fluidity. Thus 2FeO. $\text{SiO}_2$ , with  $\text{SiO}_2$  29.20 and FeO 70.80 per cent., reduced to a total of 95, gives  $\text{SiO}_2$  27.74 and FeO 67.26, leaving 5 per cent. for other oxides; in the same manner, 3FeO.2 $\text{SiO}_2$ , with  $\text{SiO}_2$  35.70 and FeO 64.30 per cent., gives  $\text{SiO}_2$  33.915, FeO 61.085, RO 5.000 per cent.; and the 4RO.3 $\text{SiO}_2$ , with  $\text{SiO}_2$  38.46 and FeO 61.54 per cent., gives  $\text{SiO}_2$  36.537, FeO 58.463, RO 5.000 per cent. With these ferrous slags, 28 per cent.  $\text{SiO}_2$  is about as low as one dares to go, 33 per cent.  $\text{SiO}_2$  is a better figure; 38 and 39 per cent.  $\text{SiO}_2$  is rather high. There is an old rule which it is safe to follow in starting: to make  $\text{SiO}_2$  about 33 per cent., to figure the iron as  $\text{Fe}=\text{SiO}_2$ , and to have about

<sup>1</sup> "General Metallurgy," 1913, p. 455; *Tr. A. I. M. E.*, 1899, XXI, 682.

10 per cent. CaO. This will give a total of 95.5 per cent. and allow 4.5 per cent. for other oxides.

Slags made in some of the few remaining copper blast-furnaces in which a strictly-reducing fusion is carried on are given in Table 28.

**100. Fuel and Blast.**—The fuel ordinarily used is coke; a common ratio is 6 charge : 1 coke, which is equal to 14 per cent. coke; this figure sometimes falls to 13 and again rises to 17 per cent. An overheating of a ferruginous slag by an excessive amount of coke is likely to cause reduction of iron to the metallic state. The furnace runs best if it has just the right amount of fuel; any lack will cause the forming of long noses at the tuyères and a corresponding reduction of tonnage.

Charcoal, which used to be the universal blast-furnace fuel, has been given up in practically all non-ferrous blast-furnaces.<sup>1</sup> Where one is forced to use it, the amount required may be one-third larger than the necessary coke.

In a few instances green wood<sup>2</sup> sawed into 2-ft. lengths has been successfully used to replace as much as  $\frac{1}{2}$  of the coke, 1 lb. coke being equal to from 2.6 to 3.0 lb. wood.

Experiments with oil as blast-furnace fuel have been carried on by Hamilton<sup>3</sup> Kiddie,<sup>4</sup> Waters,<sup>5</sup> and Lang.<sup>6</sup>

The blast in a reducing fusion is hardly ever preheated; in some instances,<sup>7</sup> as with the Giroux hot-blast, Figs. 197–198,<sup>8</sup> part of the heat of the tunnel-head gases is utilized for this purpose or the Kiddie hot-blast system.<sup>9</sup>

The blast-pressure will vary greatly with the width of the furnace, the diameter and number of tuyères, the amount of fines in the charge and the percentage of iron. Formerly a pressure of 12 oz. per square inch was common; with the increase of distance between tuyères this figure has grown materially (see Table 28).

Lloyd<sup>10</sup> gives as his experience of smelting at Cerro de Pasco, Peru, altitude 14,000, that a blast-furnace behaves about the same way as at sea-level, except that its smelting power is smaller; that with slag-composition the same holds good; that any pyritic effect (§ 104) is lower; that on account of the diminished smelting power radiation losses are to be avoided (no jacketing of crucible walls), the tuyères should be of larger diameter and the distance (or width of furnace) smaller, and the coke of good quality.

<sup>1</sup> Modern exception: C. S., *Eng. Min. J.*, 1911, XCI, 110.

<sup>2</sup> *Trans. A. I. M. E.*, 1891, XX, 545 (Lang); *Eng. Min. J.*, 1902, LXXIV, 646 (Collins); 1906, LXXXII, 700 (Mitchell); 837 (Bromly); 1013 (Bretherton); 1910, LXXXIX, 774 (Bretherton).

<sup>3</sup> *Eng. Min. J.*, 1911, XCI, 224.

<sup>4</sup> *Op. cit.*, 1911, XCII, 434 (Jacobs).

<sup>5</sup> *Op. cit.*, 1912, XCIII, 877.

<sup>6</sup> *Min. Sc. Press*, 1913, CVI, 248.

<sup>7</sup> Bretherton, *Eng. Min. J.*, 1899, LXVIII, 604, 698; 1900, LXIX, 614; LXX, 760; *Min. Sc. Press*, 1900, LXXXI, 572, 1912, CIV, 243.

<sup>8</sup> Traylor Engineering Co., *Eng. Min. J.*, 1906, LXXXII, 698; *Min. Sc. Press*, 1906, XCIII, 792. Vail, *Eng. Min. J.*, 1913, XCVI, 341 (United Verde Copper Co.).

<sup>9</sup> Jacobs, *Eng. Min. J.*, 1906, LXXXII, 598.

<sup>10</sup> *Tr. Met. Inst. Min. Met.*, 1909–10, I, 11.

Sacio<sup>1</sup> concludes from his study of smelting at high altitudes, that the capacity of blowers, air-conduits, and tuyères has to be increased; that effort has to be made to diminish the loss by radiation; and that the use of hot blast is desirable.

**101. Chemistry of Reducing Smelting.**—The details of the chemistry of the reducing fusion of roasted sulphide copper ore have been studied little. In general, the processes to be considered are reduction, sulphurization, decomposition, and slagging; oxidation is confined practically to the burning of the fuel although some sulphide may be attacked by free O. The principal reducing agents are C and CO.

(1) Reduction may be expressed by  $2\text{CuO} + \text{C} = 2\text{Cu} + \text{CO}_2$ ,  $\text{CuO} + \text{CO} = \text{Cu} + \text{CO}_2$ ,  $2\text{CuSO}_4 + 3\text{C} = \text{Cu}_2\text{S} + \text{SO}_2 + 3\text{CO}_2$ ;  $\text{Fe}_x\text{O}_y + y\text{C} = \text{Fe}_x + y\text{CO}$  beginning at  $400^\circ\text{C}$  and  $\text{Fe}_x\text{O}_{x+y} + y\text{CO} = x\text{FeO} + y\text{CO}_2$  beginning at  $200^\circ\text{C}$ ;  $\text{CaSO}_4 + 4$  (or  $2$ )  $\text{C} = \text{CaS} + 4\text{CO}$  (or  $2\text{CO}_2$ ) and  $\text{CaSO}_4 + 4\text{CO} = \text{CaS} + 4\text{CO}_2$  beginning at  $700^\circ\text{C}$ ; similarly BaS from  $\text{BaSO}_4$  by C beginning at  $600^\circ\text{C}$ ., and by CO at  $650^\circ\text{C}$ .

(2) Sulphurization by  $2\text{Cu} + \text{FeS} \rightleftharpoons \text{Cu}_2\text{S} + \text{Fe}$ ,  $\text{Cu}_2\text{O} + \text{FeS} = \text{Cu}_2\text{S} + \text{FeO}$ ,  $\text{Cu}_4\text{SiO}_4 + 2\text{FeS} = 2\text{Cu}_2\text{S} + \text{Fe}_2\text{SiO}_4$ ,  $\text{Cu}_2\text{O} + \text{Ca}(\text{Ba})\text{S} = \text{Cu}_2\text{S} + \text{Ca}(\text{Ba})\text{O}$ .

(3) Decomposition of  $\text{MSO}_4$  by  $\text{MSO}_4 + \text{heat} = \text{MO} + \text{SO}_3(\text{SO}_2 + \text{O})$ ; of (Alk. earth) $\text{SO}_4$  by  $\text{Ca}(\text{Ba})\text{SO}_4 + \text{SiO}_2 = \text{Ca}(\text{Ba})\text{SiO}_3 + \text{SO}_2 + \text{O}$  beginning at about  $1000^\circ\text{C}$ .

(4) Slagging has been referred to on page 179.

(5) Matting and slagging by  $4\text{CuO} + 3\text{FeS} + \text{SiO}_2 + 2\text{C} = 2\text{Cu}_2\text{S}, \text{FeS} + \text{Fe}_2\text{SiO}_4 + 2\text{CO}$ .

Before considering the changes in the ascending gas-current, it is necessary to picture the conditions of the charge extending from tuyère to throat. In the smelting zone coke will prevail over melting refractory parts of the charge requiring the high temperature of this region to become liquified; matte and eutectiferous constituents of the reduced original charge have been melted above and have run down below the tuyère-level. Higher up, the relative amounts of fuel and charge will be approximately the same as when fed at the throat. The temperature at the tuyères of about  $1200^\circ\text{C}$ . will decrease toward the top of the charge from which the gases leave at a temperature of  $250^\circ\text{C}$ . or higher.

The blast entering through the tuyères strikes coke at a temperature of  $1200^\circ\text{C}$ . According to Ernst<sup>2</sup> the C burns to CO, but the large volume of air entering oxidizes the CO in part to  $\text{CO}_2$ , so that at the tuyère-level the gases are a mixture of N,  $\text{CO}_2$ , and CO. As they ascend in the furnace they arrive quickly at the region of lower temperature; the reducing power of C, burning now to  $\text{CO}_2$ , and that of CO, also burning to  $\text{CO}_2$ , increase as long as this power is not weakened by the increasing presence of  $\text{CO}_2$ . On the whole the percentage of  $\text{CO}_2$  in the gas-mixture becomes larger as this rises in the furnace, and will strongly prevail over CO when it leaves the top of the charge. The older gas

<sup>1</sup> *School Min. Quart.*, 1913, XXIV, 344; *Mel. Chem. Eng.*, 1913, XI, 499.

<sup>2</sup> Hofman, "General Metallurgy," 1913, p. 294.

analyses of Bunsen,<sup>1</sup> Kersten,<sup>2</sup> Schubin,<sup>3</sup> and Heine<sup>4</sup> appear to substantiate this; modern analyses are wanting. The gases from the blast-furnaces at Mansfeld, Germany (Table 29), form an exception, as the furnaces are run more in the manner of producing pig-iron than of matte; in fact, part of the gases is used to preheat the blast, the rest in gas engines.

TABLE 29.—TUNNEL-HEAD GASES FROM MANSFELD<sup>5</sup>

Name of smeltery	Krug	Koch	Eckhardt	Kupfer-hammer
CO <sub>2</sub>	9.3	11.1	13.6	15.6
CO	18.8	20.6	15.2	12.8
N (diff.)	71.9	68.3	71.2	71.7

Considering the changes in the descending ore-charge, at first any H<sub>2</sub>O present will be expelled, then CuO will be reduced and sulphurized, CuSO<sub>4</sub> decomposed or reduced, CuSiO<sub>4</sub> converted into Cu<sub>2</sub>O and Cu<sub>2</sub>S lower down in the furnace; incidentally reverberatory furnace reactions  $\text{Cu}_2\text{S} + \text{Cu}_2\text{O} = 4\text{Cu} + \text{SO}_2$  may occur and leave Cu to be sulphurized. In the upper part of the furnace porous Fe<sub>2</sub>O<sub>3</sub> will be reduced both by C and CO to FeO, and this lower down will either combine with SiO<sub>2</sub> or be reduced by C to Fe and then sulphurized; FeSO<sub>4</sub> will be decomposed near the throat without being reduced. Reduction and sulphurization progress as the charge sinks in the furnace. Slag-formation begins only a short distance above the tuyère-level. The Cu<sub>2</sub>S–FeS mixture of lowest melting-point fuses between 850 and 900° C. and runs downward, is to a small extent oxidized by the O of the blast, gives up some of its Fe to form slag, and collects below the tuyère-level; the rest of the sulphide melts at a slightly higher temperature and follows the first. The melting of the last sulphide is coincident with the lowest slag-formation. In this the eutectic mixture will form, soften, and fuse first; flow downward; and gradually dissolve the less fusible parts. Every charge-component passing through the hot tuyère-region filled to a great extent with incandescent coke is melted; below it, take place the separation of matte- and slag-particles, the adjustments of matte-components to form the desired matte, and of slag components to form the desired slag. Matte trickling through fused slag sulphurizes slagged copper and carries down with it the Cu<sub>2</sub>S formed, thus cleaning the slag. Any Zn in the charge is either volatilized, or enters the slag both as ZnO and ZnS, or the matte, and causes imperfect separation of matte and slag. Precious metals go with the matte, as

<sup>1</sup> *Poggend. Ann.*, 1840, L, 81, 637.

<sup>2</sup> *Berg. Hüttenm. Z.*, 1844, III, 137.

<sup>3</sup> *Op. cit.*, 1846, v, 569.

<sup>4</sup> *Bergwerksfreund*, 1843, v, 208, VI, 513, 1844, VII, 547; cited by C. F. Rammelsberg in his "Lehrbuch der Chemischen Metallurgie," Lüderitz, Berlin, 1865, p. 308.

<sup>5</sup> "Der Kupferschieferbergbau und der Hüttenbetrieb," Mansfeld'sche Kupferschieferbauende Gewerkschaft, Eisleben, 1889, p. 81.



does most of the Pb; As and Sb are volatilized and enter the matte if present in small quantities; with considerable amounts a speise may be formed.<sup>1</sup>

**102. Calculation of Charge.**<sup>2</sup>—Of the different methods of calculating charges the one based upon the production of a slag of a given silicate-degree is chosen here, as it serves for the large range of composition of the slags that are made in a reducing as well as a pyritic fusion. Another method based upon a slag of definite percentage composition is given in § 115.

The slag is to be a singulo-silicate; the factors necessary for the computation of bases and SiO<sub>2</sub> to form silicates are given in Table 30.<sup>3</sup>

TABLE 30.—COMPUTATION OF BASES AND SILICA REQUIRED TO FORM SILICATES

1 lb. base requires lb. SiO <sub>2</sub> to form a			Name of base	1 lb. SiO <sub>2</sub> requires lb. base to form a		
Singulo-silicate	Sesqui-silicate	Bi-silicate		Singulo-silicate	Sesqui-silicate	Bi-silicate
0.535	0.803	1.070	CaO	1.86	1.24	0.93
0.196	0.294	0.392	BaO	5.10	3.40	2.55
0.750	1.125	1.500	MgO	1.33	0.88	0.66
0.873	1.310	1.747	Al <sub>2</sub> O <sub>3</sub>	1.14	0.76	0.57
0.416	0.625	0.883	FeO	2.40	1.60	1.20
0.422	0.633	0.845	MnO	2.36	1.57	1.18

The analyses of ores, fluxes, and fuel are assembled in Table 31, which gives the summary of the calculation. The ore for which the charge is to be calculated is a low-grade basic roasted sulphide copper ore; there are available a high-grade siliceous oxide copper ore to furnish the SiO<sub>2</sub> that is necessary, and a roasted gold-bearing pyrite which is to be used to combine with the excess-sulphur of the roasted ore. The weight of the charge is to be 1000 lb. and the amount of coke used 14 per cent.

(1) SiO<sub>2</sub> AVAILABLE IN 100 LB. SILICEOUS COPPER ORE.

15 lb. FeO  $\times$  0.416 = 6.2 lb. SiO<sub>2</sub> required

8 lb. CaO  $\times$  0.535 = 4.3 lb. SiO<sub>2</sub> required

3 lb. MgO  $\times$  0.750 = 2.3 lb. SiO<sub>2</sub> required

9 lb. Al<sub>2</sub>O<sub>3</sub>  $\times$  0.873 = 7.9 lb. SiO<sub>2</sub> required

Total,	20.7 lb. SiO <sub>2</sub> required
	43.0 lb. SiO <sub>2</sub> present

Remain,	22.3 lb. SiO <sub>2</sub> available for fluxing purposes.
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<sup>1</sup> G. C. McMurtry, "Smelting antimonial concentrates," *Tr. Int. Min. Met.*, 1913, XXII, 50; *Min. Eng. World*, 1913, XXXVIII, 9.

<sup>2</sup> Furman, *School Min. Quart.*, 1896, XVIII, 1.

Barbour, *Min. Sc. Press*, 1909, XCIX, 664.

Mostowitsch, *Metallurgie*, 1912, IX, 559.

<sup>3</sup> Hofman, "General Metallurgy," 1913, p. 435.

TABLE 31.—CALCULATION OF CHARGE, SUMMARY

Charge-component		SiO <sub>2</sub>		FeO		CaO		MgO		Al <sub>2</sub> O <sub>3</sub>		S		Cu	
Name	Wt., pounds	Per cent.	Wt.	Per cent.	Wt.	Per cent.	Wt.	Per cent.	Wt.	Per cent.	Wt.	Per cent.	Wt.	Per cent.	Wt.
Roasted sulphide copper ore.	1000	25.0	250.0	49.0	490.0	3.0	30.0	4.0	40.0	7.0	70.0	5.0	50.0 (42.5)	2.0	20.0
Siliceous oxide copper ore ..	273 99	43.0	160.0	15.0	55.8	8.0	29.8	3.0	11.2	9.0	33.5	.....	.....	12.0	44.6
Roasted pyrite.....	92	4.0	3.7	80.0	5.1 <sup>1</sup>	.....	.....	.....	.....	2.0	1.8	3.0	2.8	.....	.....
Limestone.....	79	2.0	1.6	.....	.....	53.0	41.9	1.0	0.8	1.0	0.8	.....	.....	.....	.....
Coke ash.....	(28)	30.0	8.4	31.0	8.7	8.0	2.2	.....	.....	16.0	4.5	.....	.....	.....	.....
Total.....	1543	.....	423.7	.....	559.6	.....	103.9	.....	52.0	.....	110.6	.....	45.3	.....	64.6
Slag.....	.....	33.8	.....	44.8	.....	8.3	.....	4.2	.....	8.8	.....	.....	.....	.....	.....

<sup>1</sup> The remainder goes to matte.

(2)  $\text{FeO}$  AVAILABLE IN 100 LB. ROASTED PYRITE.

$$2 \text{ lb. Al}_2\text{O}_3 \times 0.873 = 1.7 \text{ lb. SiO}_2 \text{ required}$$

$$4.0 \text{ lb. SiO}_2 \text{ present}$$


---

Remain,            2.3 lb.  $\text{SiO}_2$  requiring  $\text{FeO}$

$$2.3 \text{ lb. SiO}_2 \times 2.4 = 5.5 \text{ lb. FeO required for SiO}_2$$

$$3.0 \text{ lb. S} \times \frac{9}{4} = 6.7 \text{ lb. FeO required to combine with S present forming FeS}$$


---

Total,            12.2 lb.  $\text{FeO}$  required

80.0 lb.  $\text{FeO}$  present

---

Remain,            67.8 lb.  $\text{FeO}$  available to form  $\text{FeS}$  with excess—S of roasted ore.

(3)  $\text{CaO}$  AVAILABLE IN 100 LB. LIMESTONE.

$$1 \text{ lb. Al}_2\text{O}_3 \times 0.873 = 0.9 \text{ lb. SiO}_2 \text{ required}$$

$$1 \text{ lb. MgO} \times 0.750 = 0.8 \text{ lb. SiO}_2 \text{ required}$$


---

Total            1.7 lb.  $\text{SiO}_2$  required for bases other than  $\text{CaO}$

2.0 lb.  $\text{SiO}_2$  present

---

Remain,            0.3 lb.  $\text{SiO}_2$  to be fluxed by  $\text{CaO}$ .

$$0.3 \text{ lb. SiO}_2 \times 2.4 = 0.7 \text{ lb. CaO required}$$

$$53.0 \text{ lb. CaO present}$$


---

Remain,            52.3 lb.  $\text{CaO}$  available for fluxing.

(4)  $\text{SiO}_2$  REQUIRED FOR FLUXING 100 LB. ROASTED ORE.

$$19 \text{ lb. FeO} \times 0.416 = 20.5 \text{ lb. SiO}_2 \text{ required}$$

$$3 \text{ lb. CaO} \times 0.535 = 1.6 \text{ lb. SiO}_2 \text{ required}$$

$$4 \text{ lb. MgO} \times 0.750 = 3.0 \text{ lb. SiO}_2 \text{ required}$$

$$7 \text{ lb. Al}_2\text{O}_3 \times 0.873 = 6.1 \text{ lb. SiO}_2 \text{ required}$$


---

Total,            31.1 lb.  $\text{SiO}_2$  required

25.0 lb.  $\text{SiO}_2$  present

---

Remain,            6.1 lb.  $\text{SiO}_2$  to be added

or for 1000 lb. ore 61 lb.  $\text{SiO}_2$ . 100 lb. siliceous ore (see 1) have available 22.3 lb.  $\text{SiO}_2$ ; hence  $100 : 22.3 = x : 61$ ,  $x = 273$  lb. siliceous ore are necessary.

## (5) ROASTED PYRITE REQUIRED FOR COMBINING WITH S IN ROASTED ORE.

$$50.0 \text{ lb. S present}$$

$$7.5 \text{ lb. S oxidized (= 15 per cent.)}$$


---

42.5 lb. S remaining to form matte

Composition of matte: Cu 40, Fe 32, S 28 per cent.

Now  $S:Fe = 28:32 = 42.5:x$

$x = 48.6$  lb. Fe = 62.5 lb. FeO

Roasted pyrite contains 67.8 lb. available FeO.

$100:67.8 = x:62.5$

$x = 92$  lb. roasted pyrite

(6) MATTE TO BE FORMED.—The 1000 lb. of roasted sulphide ore contain 50 lb. S; assuming a loss of 15 per cent. by oxidation, there remain 42.5 lb. S to form matte. There are present from the roasted ore 20 lb. Cu, and from the siliceous oxide ore  $0.12 \times 273 = 32.8$  lb. Cu; or  $20 + 32.8 = 52.8$  lb. Cu. It is desired to produce a matte containing about Cu 40, Fe 32, S 28 per cent. The 45.3 lb. S in the roasted ore and roasted pyrite would form 161.8 lb. matte containing 64.7 lb. Cu. There are present only 52.8 lb., hence 11.9 lb. have to be added. The siliceous oxide ore necessary to furnish these 11.9 lb. Cu is  $100:12 = x:11.9$ ,  $x = 99$  lb. The 99 lb. (see 1) contain  $99 \times 0.223 = 22.1$  lb. excess  $SiO_2$  which are to be slagged with CaO; the CaO required is  $22.1 \times 1.86 = 41.1$  lb. As 100 lb. limestone (see 3) contain 52.3 lb. available CaO, there will be required,  $100:52.3 = x:41.1$ ,  $x = 79$  lb. limestone.

(7) COKE AND COKE-ASH.—The coke required is 14 per cent. of the weight of the charge, or  $1543 \times 0.14 = 216$  lb., which with 13 per cent. ash furnish  $216 \times 0.13 = 28$  lb. ashes. The fluxes necessary for 100 lb. coke-ashes are found as follows:

31 lb. FeO  $\times 0.416 = 12.9$  lb.  $SiO_2$  required

8 lb. CaO  $\times 0.535 = 4.3$  lb.  $SiO_2$  required

16 lb.  $Al_2O_3 \times 0.873 = 13.9$  lb.  $SiO_2$  required

Total,	31.1 lb. $SiO_2$ required
	30.0 lb. $SiO_2$ present

Remain,	1.1 lb. $SiO_2$ in excess,
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which can be neglected, the coke-ash being practically self-fluxing.

(8) REDUCTION OF CALCULATED WEIGHTS.—The reduction of the calculated weights of 1543 lb., required by 1000 lb. roasted ore to 1000 lb. charge, is obtained by the charge-factor 0.648, which is found by  $1543x = 1000$ ,  $x = 0.648$ . The charge of 1000 lb. will be made up of

Roasted ore,  $1000 \times 0.648 = 648$  lb.

Siliceous ore,  $372 \times 0.648 = 241$  lb.

Roasted pyrite,  $92 \times 0.648 = 60$  lb.

Limestone,  $79 \times 0.648 = 51$  lb.

Total,	= 1000 lb.
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(9) **PERCENTAGE COMPOSITION OF SLAG.**—The percentage composition of the slag made is determined by the slag-factor, Table 31 ( $423.7 \text{ SiO}_2 + 559.6 \text{ FeO} + 103.9 \text{ CaO} + 52.0 \text{ MgO} + 110.6 \text{ Al}_2\text{O}_3 = 1250$ , and  $1250x = 100$ ).  $x = 0.08$ . The slag is therefore  $\text{SiO}_2$  33.8,  $\text{FeO}$  44.8,  $\text{CaO}$  8.3,  $\text{MgO}$  4.2,  $\text{Al}_2\text{O}_3$  8.8 per cent.; it will form  $1543 : 1250 = 100 : x$ ,  $x = 81$  per cent. of the weight of the charge. The 161.8 lb. matte present will form approximately 10.5 per cent. of the charge, the remaining 9.5 per cent. are O,  $\text{CO}_2$ , and  $\text{SO}_2$ .

**103. Management and Results.**—The management of the furnace is practically the same as that of the partial pyritic furnace, given in §114; it is passed over here.

As regards the elimination of As, Sb, and Bi, Gibb<sup>1</sup> gives an example in which, with a roasted ore containing Cu 10.60, As 0.102, Sb 0.025, Bi 0.01 per cent., there was eliminated by volatilization and scorification in smelting for a 33 per cent. copper matte, of the As 26.1, the Sb 27.1, and the Bi 51.0 per cent.

The heat-efficiency of the operation is from 65 to 70 per cent.

The loss in copper endured is that carried off by the slag and the gases; the slag-loss at present is under 0.4 per cent.; the gas-loss varies too greatly to permit giving any figure.

An account of stock and a thermal balance will be given in connection with the reducing smelting of a roasted sulphide Ni-Cu ore (§116), as modern examples are available, which is not the case with Cu ore.

The working results of a few examples of practice are given in Table 28.

## (b) PYRITIC SMELTING

### 104. Pyritic and Partial Pyritic Smelting of Raw Sulphide Ore for Matte.<sup>2</sup>—

Pyritic smelting is a process in which the oxidation of pyritic ore furnishes the heat necessary to carry on the operation; the leading exothermic reaction is  $2\text{FeS} + \text{SiO}_2 + \text{O}_6 = 2\text{FeO} \cdot \text{SiO}_2 + 2\text{SO}_2$ . Partial pyritic smelting is one in which the deficiency of pyritic ore is made up by addition of carbonaceous fuel to the charge; the lack of heat by the pyritic reaction is supplemented by that of

<sup>1</sup> *Tr. A. I. M. E.*, 1903, XXXIII, 657.

<sup>2</sup> T. A. Rickard, "Pyrite Smelting," reprint of articles published in the *Engineering and Mining Journal*, 1903–1905; Sticht, "History of Pyritic Smelting," *Tr. Austr. Inst. Min. Eng.*, 1906, XI, 1; "Pyritic Smelting," *Metallurgie*, 1906, III, 105, 149, 222, 256, 265, 386; E. D. Peters, "Principles of Copper Smelting," 1907, pp. 213–338; "Practice of Copper Smelting," 1911, 205, 243; Sticht, "Mining and Smelting at Mount Lyell," *Metallurgie*, 1906, III, 563, 591, 638, 664, 686, 709, 760, 788; *Min. Ind.*, 1907, XVI, 385–442; Kroupa, *Oest. Jahrb.*, 1904, LI, 82 (comments by Sticht in *Metallurgie*, 1906, III, 105); Carpenter, *Min. Ind.*, 1900, IX, 690, *Tr. A. I. M. E.*, 1900, XXX, 1128; Nicholls, "Pyrite Smelting at Tilt Cove," *Eng. Min. J.*, 1908, LXXXVI, 462; Alabaster-Wintle, *Tr. Inst. Min. Met.*, 1905–06, XV, 269; Guess, *Eng. Min. J.*, 1910, XC, 866; 1911, XCI, 557; 1912, XCIII, 113; 1912, XCIV, 925; Wright, *Min. Sc. Press.*, 1906, XCII, 124, 237; Pratt, *Eng. Min. J.*, 1913, XCV, 1191; Emrich, *Met. Chem. Eng.*, 1913, XI, 327; Wright, *Eng. Min. J.*, 1913, XCVI, 825; Negative Results: *Eng. Min. J.*, 1907, LXXXIV, 343 (Beardsley), 601, 603 (Lang), 1079 (Hixon), 1033 (Moore), 1130 (Fulton), 1223 (Grabill); 1908, LXXXV, 175 (Koch), 325 (Fowler), 373 (Beardsley); "Iron Sows," *Eng. Min. J.*, 1904, LXXVIII, 93 (Myers-Reybold). Guess, *Bull. Canadian Min. Inst.*, No. 24, February, 1914, p. 87.

carbon-combustion,  $C + O_2 = CO_2$ , through the O of the blast. Usually there is added to the true pyritic charge a small amount of coke, from 1 to 3 per cent., which, however, does not reach the focus (the zone of active oxidation by the blast), but is oxidized higher up in the furnace by  $SO_2$ . Pyritic furnaces have worked for days at a time without any coke whatever, hence the division between entire and partial pyritic smelting in practice is not clearly defined. However, the statement that partial pyritic smelting begins with a sufficient addition of coke to be burnt in part by the O of the air instead of the  $SO_2$  of the gases, and thus weakens the pyritic effect of the blast, comes close to the truth, and 3 per cent. coke appears to be this amount. The three essential requirements for pyritic smelting are pyritic ore, free  $SiO_2$ , and air.

Pyrite,  $FeS_2$ , loses 1 mol. S at  $700^\circ C$ . leaving behind what is practically FeS, and this upon raising the temperature above  $1200^\circ C$ .<sup>1</sup> (see curve, Fe-S, of Friedrich, in § 119), gives up some of its S, leaving behind mixtures of FeS and Fe in which the Fe increases as the temperature rises.

Silica ( $SiO_2$ ) must be free in order that it may combine readily with FeO at the moment when this is formed, as is the case in converting matte, the union being attended by evolution of heat.<sup>2</sup> Combined  $SiO_2$  is not only non-available as a heat- and slag-forming agent, being already united with a base, but is detrimental to the process in that it absorbs heat by having to be liquefied; and in pyritic smelting the excess-heat over that which is actually required is very small under the most favorable conditions.

Air has to be supplied in much larger quantities than in a reducing fusion, as the O required both by the Fe and the S is greater than that by the C of the  $13 \pm$  per cent. coke in the latter process. If both FeS and C are present in the charge, the C will pre-empt all the O it requires to form CO or  $CO_2$ , and only the excess O will be available for FeS. But the oxidation of C creates not only a high temperature where it burns, but it furnishes a hot ascending gas current which assists a premature melting of the readily fusible FeS (See § 119); the latter then runs down unoxidized through the column of coke and collects, little changed, below the level of the tuyères.

The interior of a pyritic furnace has a very different appearance from one in which C forms the heat-giving constituent. In the latter there is a slowly downward-moving charge of ore, flux, and fuel, carried more or less by the boshes and the column of coke in front of the tuyères; the jackets of the smelting zone are slightly coated with half-fused charge, and at the tuyère-level the noses of the otherwise bright tuyères are short. Vertical sections through the smelting zone show the furnace to have about the same appearance when in or out of blast. Figs. 227-228 by Freeland<sup>3</sup> represent the oval furnace, formerly used by the Ducktown Sulphur, Copper and Iron Co., Isabella, Tenn., running with 2.75 per cent. coke on a pyrrhotite ore. They show that there has been formed a bosh extending along the side- and end-walls leaving open in the center a chan-

<sup>1</sup> Le Chatelier-Ziegler, *Bull. Soc. d'Enc.*, 1902, p. 368; *Metallographist*, 1903, VI, 19.

<sup>2</sup> Hofman, "General Metallurgy," 1913, p. 101.

<sup>3</sup> *Eng. Min. J.*, 1903, LXXV, 664.

nel (converting-slit). It consists of porous friable gangue carrying the charge; its position, however, is not stationary nor its form fixed. As the furnace forms its own pyritic bosh, the question of bosh in the jackets is not of paramount importance, but rather the temperature of their cooling-water; thus at Kyshtim, Siberia, the temperature of the lower jackets is kept cool in order to obtain a pyritic bosh of the desired thickness.

The tuyères in the furnace are mostly dark, light being rarely discernible when they are punched; a bar has been driven in from one side and withdrawn from the other with the naked hand. This proves that the tuyères are bridged, that the melted charge passes downward in the spaces between them, and that the hot fusion-zone lies above. The blast, warmed and finely divided in its passage through the

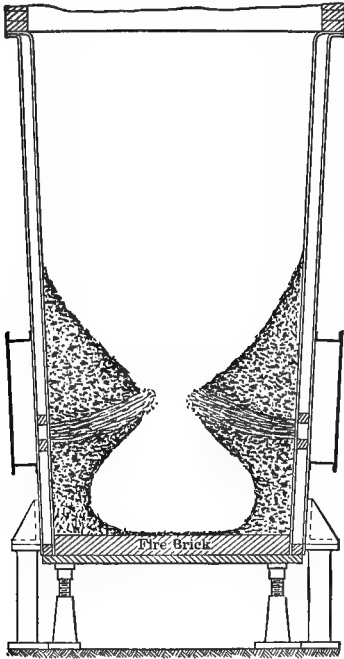


FIG. 227.—Vertical section through pyritic blast-furnace.

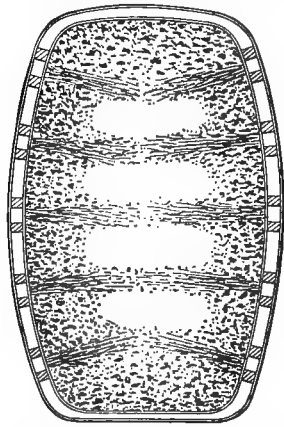


FIG. 228.—Horizontal section through pyritic blast-furnace.

porous boshes, must be delivered upward into the fusion zone against the descending streamlets of  $\text{FeS}$  and the quartz fragments of the charge, and exerts there its powerful oxidizing effect. Sticht<sup>1</sup> smelting a pyritic ore at Mount Lyell with 1.25 per cent. coke, notes a similar porous bosh which consists of quartz fragments and slag, and is free from  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ ,  $\text{CaO}$ , and particles of matte.

Partial pyritic smelting standing between true pyritic and reducing smelting will show some of the phenomena of both processes.

The first experiments in pyritic smelting are those of John Hollway<sup>2</sup> with pyrite from Rio Tinto. In 1889 L. Austin<sup>3</sup> did some work in Toston, Mont.;

<sup>1</sup> *Metallurgie*, 1906, III, 115.

<sup>2</sup> "A New Application of Bessemer's Process of Rapid Oxidation, by which Sulphides are Utilized for Fuel," Soc. of Arts, April 12, 1879.

<sup>3</sup> *Tr. A. I. M. E.*, 1887-88, XVI, 257.

in 1891 R. Sticht made the first successful runs in this country at Boulder Valley, Mont.; in 1893 the Bi-Metallic Co. ran a pyritic plant at Leadville, Colo.<sup>1</sup> The process lay dormant for a while until it received a new impetus in 1895, when Sticht introduced it at Mount Lyell, Tasmania. Since then it has grown in importance. At present entire pyritic smelting is carried on at the Mount Lyell, Ducktown, Isabella, Keswick, Mammoth, Rio Tinto, Kosaka, Sulitjelma, and probably other smelteries. Partial pyritic smelting has become very common in this country.

**105. Pyritic Smelting Proper.** (1) **THE SLAG.**—From what has been said regarding pyritic smelting, it is clear that a high formation temperature of the pyritic slag is of paramount importance for the process, as the charge has to stand unmelted to enable the blast to attack the FeS, and form FeO and SO<sub>2</sub>, when the FeO must combine instantaneously with SiO<sub>2</sub>, as in converting matte; the ferrous silicate formed will then dissolve gradually the remaining refractory slag-forming constituents of the charge and form with them the final slag.

Referring to Table 32, which gives the formation temperature of some ferrous silicates, it is seen that omitting the impossible 4RO:SiO<sub>2</sub>, the ferrous singulo-silicate 2RO:SiO<sub>2</sub> has the highest formation temperature (1270° C.); the silicate 3RO:SiO<sub>2</sub>, comes next (1140° C.); then follow the sesqui-silicate, 4RO.3SiO<sub>2</sub>, with 1120° C; and the bi-silicate, RO:SiO<sub>2</sub>, with 1110° C. The silicate-degree is then a function of the temperature, and the formation temperature falls as the silicate degree rises. The aim must be therefore to form a ferrous singulo-silicate, and the three factors, FeS, O, and SiO<sub>2</sub> have to be so balanced as to make this possible. If there is too much FeS, which is equivalent to a lack of O, there is too little oxidation; and this means lack of heat in the combustion zone, accompanied by the passage of undecomposed FeS through the blast followed by collection below the tuyère-level. If for a given amount of FeS and O, there is an excess of SiO<sub>2</sub>, this will accumulate in the shaft (silica-sow) and block the smelting; if there is a lack, some Fe will be peroxidized to Fe<sub>3</sub>O<sub>4</sub> or

TABLE 32.—FORMATION TEMPERATURE OF SOME FERROUS SILICATES<sup>2</sup>

Formula of silicate	Chemical composition		Formation temperature Deg. C.
	SiO <sub>2</sub> per cent.	FeO per cent.	
4RO SiO <sub>2</sub> .....	17.20	82.80	1280
3RO : SiO <sub>2</sub> .....	21.70	78.30	1220
2RO : SiO <sub>2</sub> .....	29.20	70.80	1270
3RO : SiO <sub>2</sub> .....	35.70	64.30	1140
4RO : 3SiO <sub>2</sub> .....	38.46	61.54	1120
RO : SiO <sub>2</sub> .....	45.45	54.55	1100

<sup>1</sup> Doolittle-Jarvis, *Tr. A. I. M. E.*, 1910, XLI, 709.

<sup>2</sup> Hofman, *Tr. A. I. M. E.*, 1899, XXIX, 682.



$\text{Fe}_2\text{O}_3$  which, taken up by the slag, decreases its fusibility and may stop the furnace. As a slag consisting solely of  $\text{SiO}_2$  and  $\text{FeO}$  does not separate well from the matte, it has to be lightened by some earthy base. The percentage of  $\text{CaO}$ , including its equivalents of  $\text{MgO}$ ,  $\text{BaO}$ ,  $\text{Al}_2\text{O}_3$ , should not be less than 10 per cent.; the usual range is 12 and 16 per cent. (see Table 28). The percentage of  $\text{Al}_2\text{O}_3$  in any case must be low; perhaps 7 per cent. is the limit, usually it does not exceed 5 per cent. The slag of Mount Lyell,<sup>1</sup>  $\text{SiO}_2$  32.47,  $\text{FeO}$  52.15,  $\text{CaO}$  4.77,  $\text{Al}_2\text{O}_3$  7.22,  $\text{BaO}$  0.90,  $\text{S}$  0.88,  $\text{Cu}$  0.39 per cent.,  $\text{Ag}$  0.189 oz. per ton, is a singulo-silicate. Other slags are given in Table 28.

**106. Fuel and Blast.**<sup>2</sup>—The rôles that fuel and blast play in pyritic smelting have been discussed in § 104. There remain the calculation of the blast required and the consideration of hot blast.

**QUANTITY OF AIR.**—The calculation of the cubic feet of air per minute required must be based upon the amount of  $\text{FeS}$  that is to be oxidized, and this is best referred to the square foot of hearth area. Assume that the smelting power of the furnace is 6 tons of charge per square foot hearth area in 24 hr., equal to 500 lb. per hour; that the charge contains 50 per cent.  $\text{FeS}_2$ ; and that this loses  $\frac{3}{4}$  of its  $\text{S}$  by sublimation. The 500-lb. charge corresponds to 250 lb.  $\text{FeS}_2$  (46.7 Fe, 53.3 per cent.  $\text{S}$ ) or 116.8 lb. Fe and 133.2 lb.  $\text{S}$ . With  $\frac{3}{4}$  of the  $\text{S}$  volatilized, this is changed to 116.8 lb. Fe and 76.1 lb.  $\text{S}$ . Let 90 per cent. of this be oxidized and 10 per cent. go to the formation of matte; the blast has to be supplied for 105.1 lb. Fe and 68.5 lb.  $\text{S}$ . Now  $\text{Fe}:\text{O}=56:16=105.1:x$ ,  $x=30.0$  lb.  $\text{O}$ ; and  $\text{S}:\text{O}_2=32:32=68.5:y$ ,  $y=68.5$ ; hence there are required  $30.0+68.5=98.5$  lb.  $\text{O}$  per hour with  $98.5 \times 3.33$  or 328.3 lb.  $\text{N}=426.8$  lb. air  $=426.8 \times 13.067$  (for  $15^\circ \text{C}$ .) or 5577 cu. ft. air per hour  $=92.9$  cu. ft. air per minute. Assuming an efficiency of 90 per cent., gives 103 cu. ft. as the amount of air required. Wright<sup>3</sup> found at Keswick, Cal., that his furnace, with a charge containing 50 per cent.  $\text{FeS}_2$  and treating 11 tons of charge per square foot hearth area in 24 hr., did good work when it received per minute per square foot hearth area 365 cu. ft. air; this would oxidize 7 lb.  $\text{FeS}_2$  per minute, and the furnace gases would contain 12 per cent. vol.  $\text{SO}_2$ .

**PREHEATING AIR BLAST.**—Heating the blast has been the subject of much discussion. The idea has been prevalent that hot blast would raise the degree of concentration of the matte. Sticht has shown that not only does it not effect this, but that the result is just the reverse, because hot-blast causing a more siliceous slag to be formed is equivalent to a lower degree of oxidation. The main reason for the higher concentration of matte with cold blast is that, in order to produce the same heat more cold air is required in a given time than hot air; the larger volume of air rises in the shaft to the point at which  $\text{FeS}$  begins to melt, and this trickling down through a longer column of hot gangue matter is exposed to oxidation for a longer period of time. At Mount Lyell the degree of concentration with hot blast was 7 into 1; it is at present with cold blast from 18

<sup>1</sup> *Min. Ind.*, 1907, XVI, 435.

<sup>2</sup> Walter, *Eng. Min. J.*, 1913, XCIII, 797.

<sup>3</sup> *Eng. Min. J.*, 1905, LXXIX, 957.

to 20 into 1, furnishing a matte with 40 per cent. Cu, and could be made greater by additional blast if this was desirable. It is believed that not a single blast-furnace doing true pyritic smelting is supplied with hot blast.

**107. Chemistry of Pyritic Smelting.**—In discussing the chemical reactions that take place in the blast-furnace it is convenient to consider separately the ascending gas-current and the descending ore-charge. The blast of atmospheric temperature upon entering the furnace at the tuyère-level comes in contact with the porous boshes and bridges, is warmed and being further heated in traveling upward through melted descending charge strikes, a short distance above, fused red hot FeS trickling downward through siliceous gangue material; it oxidizes the FeS to FeO and SO<sub>2</sub> giving up its entire O; simultaneously the FeO forms slag while the gas-mixture of N and SO<sub>2</sub> with a temperature of 1200° C. rises in the shaft and preheats the descending charge; cooled by this to 700° C. it becomes charged with S-vapor (FeS<sub>2</sub>+700° C.=FeS+S), the amount of Mount Lyell averaging 1.7 per cent. at a distance of 4 or 5 ft. below the top of the charge; the N+SO<sub>2</sub>+S-vapor rises in the furnace to the top of the charge (250° C.) where the S ignites and burns. If the temperature of the stock-line should sink below 250° C., the volatilization and ignition points of S, some S would be deposited and clog the passage of the gases. During the ascent of the gases the small amount of coke charged, <3 per cent., is consumed by the reaction SO<sub>2</sub>+C=S+CO<sub>2</sub>+27,940 cal., which assists in warming the charge. Table 33 gives analyses of Mount Lyell gases when the furnace is running normally, and Table 34 similar data when running "wild," when FeS is not being oxidized. The figures<sup>1</sup> in Table 33 show a very small amount of free O, which varies very little in

TABLE 33.—NORMAL GAS FROM PYRITIC FURNACE, MOUNT LVELL

No. of samples	Sample, distance beneath throat, feet	SO <sub>2</sub>	CO <sub>2</sub>	CO	O
5	2-2.5	6.64	5.08	0.16	0.84
4	2-2.5	7.95	3.075	none	1.50
4	2.5	8.925	5.45	none	0.70
13	2-3.5	7.88	5.93	0.02	0.35
5	3-3.5	6.12	7.86	none	0.66
14	6	8.44	4.50	none	0.4
4 <sup>2</sup>	6	9.475	3.70	none	none
1 <sup>2</sup>	6	10.60	4.40	0.2	none
5 <sup>2</sup>	6-7	7.90	3.56	none	0.88

a distance of 2 to 7 ft. below the surface of the charge, and practically no CO owing to the reaction SO<sub>2</sub>+CO=S+CO<sub>2</sub>. In other words, the O entering at the tuyères is almost wholly consumed by the oxidation of the FeS, and the small amount remaining as free O is rendered innocuous by the great dilution with

<sup>1</sup> Objections by Guess, *Eng. Min. J.*, 1912, XCIV, 925.

<sup>2</sup> From the preceding 14.

indifferent gas. As soon as the regular process is disturbed, the composition of tunnel-head gas changes (Table 34). The air rushes up through the charge effecting only little oxidation; the percentage of O in the gases is high, and that of SO<sub>2</sub> low.

TABLE 34.—ABNORMAL GAS FROM PYRITIC FURNACE, MOUNT LYELL

No. of samples	Sample, distance beneath throat, feet	SO <sub>2</sub>	CO <sub>2</sub>	CO	O
I	2	22.40	4.20	none	3.40
I	2.5	2.40	0.20	0.2	14.60
5	2.5-2.75	5.26	1.78	0.07	11.29
5	3	3.02	3.16	none	11.08
I	3	1.20	1.10	none	16.70
7	3-3.5	2.59	4.73	0.03	6.91

Following the descending ore charge, it is convenient to distinguish three zones:

(1) THE ZONE OF PREPARATORY HEATING.—The top of the charge is at 250° C., S-vapor is burning over it, and air is rushing in through the feed-doors at the rate perhaps of three times the volume of the ascending gas-current. The charge when introduced gives up quickly its hygroscopic water and more slowly that which is chemically combined; between 250 and 700° C. it absorbs heat from the gas-current and some of its coke is oxidized by the SO<sub>2</sub> of the gases; at 700° C. pyrite begins to give off 1 mol. of S. With these changes the charge passes downward, at Mount Lyell for a distance of 7 or 8 ft., whereupon it reaches the oxidizing zone (2).

(2) THE ZONE OF OXIDIZING SMELTING OR FOCUS.—This at Mount Lyell extends downward to 2 or 3 ft. above the tuyères. The altered charge, now FeS + gangue + limestone, reaches the region of 880° C. where CaCO<sub>3</sub> is dissociated; lower down the FeS begins to fuse, trickles down over the pieces of SiO<sub>2</sub> and CaO in separate droplets or in assembled rivulets, and is met by the O of the blast; the FeS is oxidized and simultaneously combines with SiO<sub>2</sub> to Fe<sub>2</sub>SiO<sub>4</sub>; this hot ferrous singulo-silicate traveling over siliceous gangue matter and CaO dissolves these in its downward course and slags them so that, arrived at the level of the tuyères, there is little of them left with exception of the silica-boshes and -bridges.

(3) THE ZONE OF ADJUSTMENT.—The melted slag-matte which descends through the more or less open spaces between the bridged tuyères collects below these. Here the different silicate mixtures form a uniform mixture, and the matte tends to separate to some extent from the slag, although it is not given sufficient time and space to accomplish this satisfactorily, as both matte and slag leave the furnace together over the blast-trapping spout. The final separation takes place in the external fore-hearth.

In the oxidation of FeS there is always left enough unaltered FeS to resulphurize any Cu that may have become oxidized in its downward course.

**108. Management and Results.**—The management of a pyritic furnace requires considerable care, as even a slight irregularity is likely to disturb the normal working. Thus *e.g.*, the matte-fall is likely to be irregular owing to the slight changes in the ore, in the moisture of the air, or in the mechanical condition of the furnace, which hinder or favor the O from doing its proper work in the focus. At the same time the character of the slag formed may not change materially although the amount will be decreased or increased.

The analyses of gases from normal work, Table 33, show only a trace of free O and as much as 12 per cent. vol. SO<sub>2</sub>; those from abnormal work, Table 34, much free O; the furnace makes a large amount of low-grade matte and a small amount of acid slag; simultaneously the focus begins to cool. Correcting the evil by addition of coke or coke- and slag-charges will heat up again the lower part of the furnaces and cause the production of much low-grade matte. Regular pyritic smelting can then be started again, just as in blowing in a pyritic furnace; where the start is made with a reducing fusion. When a furnace gets out of order, it is usually cheaper to blow it down and start fresh in an interval of 24 hr. instead of trying to doctor the patient. Thus Sticht's campaigns last about four weeks.<sup>1</sup> The operations of blowing-in, etc., which are the same as in partial pyritic smelting, are discussed in § 117.

The elimination of As, Sb, Bi, and Pb in a pyritic furnace,<sup>2</sup> is much greater than in a reducing fusion. Sticht<sup>3</sup> gives 70 per cent. as the direct efficiency of his work at Mount Lyell; 35 per cent. of the heat generated is absorbed by the chemical work of smelting and the fusion of the solid products; 35 per cent. by dissociations preceding or accompanying the chemical reaction; the balance of 30 per cent. is lost by radiation. An average of 11 years' work (including early experimental work, converting, and resmelting intermediary products), treating since 1907 ore with Cu 2.25 per cent. and producing matte with Cu 44.3 per cent., gave Sticht a yield of Cu 85.72, Ag 92.57, Au 102.28 per cent.

**109. The Knudsen Process.**<sup>4</sup>—This process, a modification of true pyritic smelting, consists in smelting intermittently with a small addition of coke and raw pyrite in a special tilting converter for matte and slag. At Sulitjelma, where it is in operation, the ores are of two kinds, siliceous (Cu 6.5, Fe 32.8, S 36.8, SiO<sub>2</sub> 16.5, Al<sub>2</sub>O<sub>3</sub> 9.3 per cent.) giving a fluid, and schistose (Cu 5.1, Fe 26.3, S 23.9, SiO<sub>2</sub> 28.8, Al<sub>2</sub>O<sub>3</sub> 12.2 per cent.) giving a sticky slag; they are mixed and furnish a waste slag with SiO<sub>2</sub> 28–29, FeO 56–59, Al<sub>2</sub>O<sub>3</sub> 10–12, S 1.5, Cu

<sup>1</sup> Peters, "Principles," p. 305.

<sup>2</sup> Lang, *Eng. Min. J.*, 1904, LXXVIII, 461.

<sup>3</sup> *Min. Ind.*, 1907, XVI, 435.

<sup>4</sup> Schiffner, "V Internat. Kongress für Angewandte Chemie," Berlin, 1904, II, p. 112.

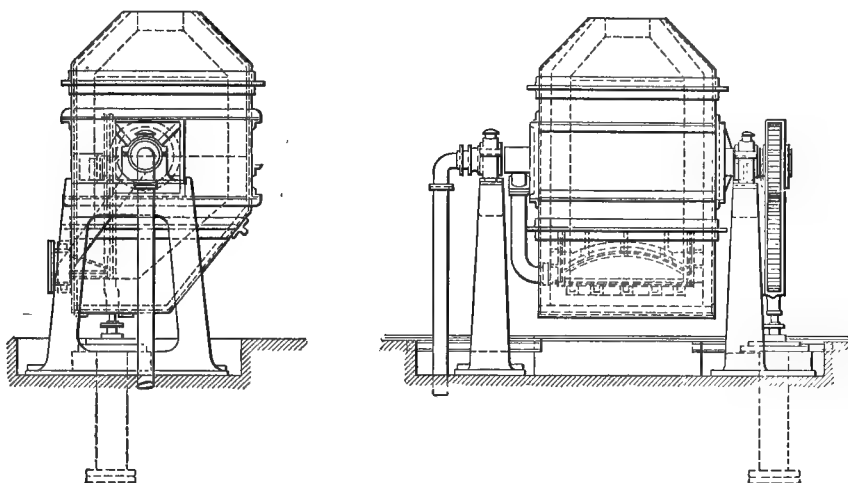
Knudsen, *Eng. Min. J.*, 1904, LXXVII, 757; *Min. Ind.*, 1903, XII, 119; 1908, XVII, 315; *Oest. Zt. Berg. Hüttenw.*, 1909, LVII, 426; 1912, LX, 568; *Eng. Min. J.*, 1909, LXXXVII, 1080. New furnace, U. S. Patent No. 1075214 Oct. 9, 1913.

Dyck, *Metallurgie*, 1907, IV, 416.

Hofman-Mostowitsch, *Tr. A. I. M. E.*, 1908, XXXIX, 652.

0.3–0.6 per cent. The ore ought not to be too fine. Charges have been run successfully with one-third coarse, one-third fine, and one-third dust.

The converter shown in Figs. 229–230, consists of three parts, a cylindrical body suspended by trunnions which are connected with the air-blast and the rotating mechanism; a conical hood; and a bottom contracted toward the blast-inlet, which is close to the bottom. The converter is lined with 10 in. of magnesite brick and has an inner diameter of 6 ft.; there are 18 tuyères  $\frac{2}{3}$  in. in diameter. In operating, the converter, at a yellow heat from the preceding charge and retaining a small amount of matte, receives a bed of coke or coal of 0.5 to 1.5 per cent. of the weight of the charge, which is sufficiently deep to extend a little above the tuyères; next the blast is started to bring the fuel to a red heat,



FIGS. 229–230.—Knudsen converter.

then 10 tons of charge are run in from a hopper, and the blast-pressure is raised to 5 lb. The pyrite is decomposed; the FeS melts and trickling down is oxidized, and at once combines with the  $\text{SiO}_2$  of the charge. After 10 min. or after the smelting has been well started, the tuyères being kept bright by punching, and the melted charge reaches the tuyère-level, the blast-pressure is raised to 10–15 and even to 22 lb. per square inch. In from 1.5 to 2 hours the charge is smelted, whereupon concentration of matte to 40–50 per cent. Cu begins; this lasts about 2 hr., making the total time required 3.5 to 4.5 hr. for the treatment of 10 tons of charge. The content of the converter is discharged into an open-hearth furnace of 15 tons capacity, lined with magnesite brick, to settle the matte which takes from 1.5 to 2 hr., whereupon waste slag with  $\text{Cu} < 0.5$  per cent. is drawn from the surface of the bath. The open-hearth furnace serves also as a reservoir for matte to be blown in the Manhès converter for blister copper with  $\text{Cu}$  99.5 per cent.

The original furnace had a capacity of 210 cu. ft. and treated 10-ton charges; the latest furnace has a volume of 350 cu. ft. and takes 20 tons of charge. The

work of the larger furnace is more regular than that of the smaller. The charge ought to contain S 25 per cent. in order to do good work. The magnesite lining is good for about 180 charges; as many as 459 charges have been smelted on one lining, which costs about \$5000.00. It has been observed that slags when basic (irony) attack the lining more quickly than when acid. As  $\text{MgFe}_2\text{O}_4$  does not form at a temperature as high as  $1500^\circ \text{C}$ ,<sup>1</sup> the corrosion must be due to the eutectic  $\text{CaO} \cdot \text{Fe}_2\text{O}_3$  which readily fuses at  $1200^\circ \text{C}$ . With a furnace of 350 cu. ft. capacity treating charges of from 20 to 25 tons there are required during the first 1.5 hr. 40 h.p.; during the next 1-1.5 hr., 80-100 h.p.; during the last hour, 150-160 and even 200 h.p. to furnish the necessary blast. The temperature of the gases measured in the flue 33 ft. from the mouth of the converter ranged from 600 to  $780^\circ \text{C}$ ; they contained from 2.5 to 11.5, average 6.5, per cent. vol.  $\text{SO}_2$  and  $\text{SO}_3$ ; with gas showing 11.5 per cent. vol.  $\text{SO}_4$  the per cent. vol. of  $\text{SO}_2$  was 9-9.5, and of  $\text{SO}_3$  2-2.5. At Sulitjelma, with two 20-ton furnaces, the cost of treatment is \$0.91 per ton of ore, excluding air-compression and repairs; adding these two items gives a total of \$1.25. Attention may be called to the tremendous power-consumption of the process, which makes it suited only for localities where water-power is extremely cheap, as, e.g., in Norway (\$4.00 per horse-power year).

As a matter of record may be mentioned the various attempts of Garretson<sup>2</sup> to smelt sulphide copper ore and convert the matte formed in a single furnace. Similar experiments were made at Great Falls, Mont., in 1895<sup>3</sup> with the so-called Charles Allen process of bessemerizing in the blast-furnace crucible, which also were unsuccessful.

### C. PARTIAL PYRITIC SMELTING

**110. Partial Pyritic Smelting of Raw Sulphide Ore for Matte.**—The essential requirements for entire pyritic smelting were, massive pyritic ore containing free  $\text{SiO}_2$  and little  $\text{Al}_2\text{O}_3$  and other bases. Such ores are not of frequent occurrence; most sulphide copper ores contain pyritic material disseminated through a gangue which is likely to run high in  $\text{Al}_2\text{O}_3$ . They are treated raw by partial pyritic smelting, a process in which the lack of heat from the oxidation of insufficient  $\text{FeS}$  is supplied by the use of carbonaceous fuel, and, in addition, sometimes by preheating the blast.

**111. The Slag.**—In pure pyritic smelting, the slags made are singular silicates high in  $\text{FeO}$  and low in  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$ ; in the partial process they run high in  $\text{SiO}_2$ , low in  $\text{FeO}$ , high in  $\text{CaO}$ , and are likely to contain considerable amounts of  $\text{Al}_2\text{O}_3$ . Examples of slag compositions are shown in Table 28. Temperatures of slags as flowing from the blast-furnace measured by Clevenger<sup>4</sup> cover a range of  $1123$ – $1261^\circ \text{C}$ . The part  $\text{Al}_2\text{O}_3$  plays in these

<sup>1</sup> Hofman-Mostowitsch, *loc. cit.*

<sup>2</sup> *Min. Ind.*, 1902, XI, 206; *Eng. Min. J.*, 1908, LXXXV, 776, 1063; 1909, LXXXVIII, 1266.

<sup>3</sup> Church, *Tr. A. I. M. E.*, 1913, XLVI, 426.

<sup>4</sup> *Met. Chem. Eng.*, 1913, XI, 447.

slags is often of great importance.<sup>1</sup> In general, Vogt has found<sup>2</sup> that in slags with less than  $\text{SiO}_2$  43 per cent. and moderate amounts of  $\text{Al}_2\text{O}_3$  (ratio,  $3 \text{ CaR} (= \text{Fe.Mg.Mn}) : \text{Al}_2 > 1$ ), the  $\text{Al}_2\text{O}_3$  will act as a base. Lloyd<sup>3</sup> found in partial pyritic smelting that when the  $\text{SiO}_2$ -content of the slag exceeded 44 per cent.,  $\text{Al}_2\text{O}_3$  began to act as an acid and make the slag bad. Hofman<sup>4</sup> has shown that if in the singulo-silicate with  $\text{SiO}_2$  32.10,  $\text{FeO}$  35.90,  $\text{CaO}$  32.00 per cent. and a formation temperature of  $1150^\circ \text{C.}$ , the  $\text{SiO}_2$  is replaced by  $\text{Al}_2\text{O}_3$ , the formation temperature rises, that if the  $\text{CaO}$  is similarly replaced, the formation temperature falls slightly. If therefore both  $\text{SiO}_2$  and  $\text{CaO}$  are replaced by  $\text{Al}_2\text{O}_3$ , the formation temperature is likely to remain constant. This corresponds in part to the practice usual with a high- $\text{CaO}$  slag, of lowering the percentage of  $\text{SiO}_2$  with an increase in that of  $\text{Al}_2\text{O}_3$ . Some furnace-men assume that  $\text{Al}_2\text{O}_3$  acts always as an acid, add the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , and figure their charge to form a bi-silicate slag; others neglect the presence of  $\text{Al}_2\text{O}_3$ , and figure their slag as being made up of a mixture of a bi-silicate of lime,  $\text{CaO SiO}_2$ , and a singulo-silicate of iron  $2\text{FeO. SiO}_2$ . Table 35, by C. S. Witherell, gives the amounts of  $\text{FeO}$  and  $\text{SiO}_2$  necessary for slags with from 10 to 25 per cent.  $\text{CaO}$ , for a range of the total of the constituents of from 90 to 100 per cent.

Magnetite ( $\text{Fe}_3\text{O}_4$ ) as a flux<sup>5</sup> is undesirable in partial pyritic smelting, as the reducing power of the ascending gas-current is too weak to complete the reduction to  $\text{FeO}$  by solid C; hence  $\text{Fe}_3\text{O}_4$  is likely to enter the slag and reduce its fusibility and fluidity, as well as to be taken up by the matte. The presence of  $\text{Fe}_2\text{O}_3$  in some slags is explained by Wright<sup>6</sup> as due to the reaction  $\text{FeS} + 10\text{Fe}_2\text{O}_3 = 7\text{Fe}_3\text{O}_4 + \text{SO}_2$ . According to Hofman<sup>7</sup> the percentage of  $\text{Fe}_3\text{O}_4$  in a slag is governed by the percentage of  $\text{SiO}_2$  to which it is indirectly proportional.<sup>8</sup>

**112. Fuel and Blast.**—In § 104 the line of separation between entire and partial pyritic smelting was provisionally drawn at 3 per cent. coke. In Table 28 the amount of coke used in partial pyritic smelting is seen to be about 8 per cent. and upward of the weight of the charge. The less the weight of coke required to furnish the heat necessary for smelting, the larger will be the amount of O available for  $\text{FeS}$  in a given volume of blast. The percentage of coke required can be diminished by heating the blast,<sup>9</sup> with the result that the pyritic effect

<sup>1</sup> *Eng. Min. J.*, 1908, LXXXVI, 107, 177 (Heberlein); 264, 270 (Shelby); 483 (Bretherton); 730 (Koch); 1111 (Hooper); 1909, LXXXVII, 222 (Beardsley).

<sup>2</sup> Smith, *Eng. Min. J.*, 1910, XC, 1261.

<sup>3</sup> Peters, *Min. Ind.*, 1909, XVIII, 245.

<sup>4</sup> *Tr. A. I. M. E.*, 1899, XIX, 717; "General Metallurgy," 1913, p. 461.

<sup>5</sup> *Eng. Min. J.*, 1907, LXXXIII, 817 (Wells); 1909, LXXXVII, 962 (Bennetts); LXXXVIII, 367 (Rizo); 742 (Shelby).

<sup>6</sup> *Eng. Min. J.*, 1913, XCVI, 825.

<sup>7</sup> *Min. Ind.*, 1913, XXII, under "Lead."

<sup>8</sup> See § 119,  $\text{Fe}_3\text{O}_4$  in Matte; and § 176, Great Falls basic converter.

<sup>9</sup> *Eng. Min. J.*, 1902, LXXIII, 525 (Grabill); 1906, LXXXII, 598 (Kiddie), 698 (Giroux); 1907, LXXXII, 692. *Min. Sc.*, 1908, LVII, 46 (Parry). *Min. J.*, 1908, LXXXIII, 113 (Moore). *Electrochem. Met. Ind.*, 1906, IV, 420 (Giroux). *Tr. A. I. M. E.*, 1904, XXXIV, 422 (Bretherton) See Hofman, "General Metallurgy," § 321 and following.

TABLE 35.—SLAG COMPOSITIONS:  $x(\text{CaO} \cdot \text{SiO}_2) + y(\text{FeO} \cdot 2\text{S} \cdot \text{O}_2)$   
 $g \cdot \text{SiO}_2 = g \cdot 1.07 \text{ CaO} + g \cdot 0.416 \text{ FeO}$

Total, 80			82		84		86		88		90		92		94		96		98		100	
CaO	FeO	SiO <sub>2</sub>	FeO	SiO <sub>2</sub>	FeO	SiO <sub>2</sub>	FeO	SiO <sub>2</sub>	FeO	SiO <sub>2</sub>	FeO	SiO <sub>2</sub>	FeO	SiO <sub>2</sub>	FeO	SiO <sub>2</sub>	FeO	SiO <sub>2</sub>	FeO	SiO <sub>2</sub>	FeO	SiO <sub>2</sub>
10.0	41.9	28.1	43.3	28.7	44.7	29.3	46.1	29.9	47.5	30.5	48.9	31.1	50.4	31.6	51.8	32.2	53.2	32.8	54.6	33.4	56.0	34.0
11.0	40.4	28.6	41.1	29.2	43.2	29.8	44.6	30.4	46.0	31.0	47.4	31.6	48.9	32.1	50.3	32.7	51.7	33.3	53.1	33.9	54.5	34.5
12.0	38.9	29.1	40.3	29.7	41.7	30.3	43.1	30.9	44.5	31.5	45.9	32.1	47.4	32.6	48.8	33.2	50.2	33.8	51.6	34.4	53.0	35.0
13.0	37.5	29.5	38.9	30.1	40.3	30.7	41.7	31.3	43.1	31.9	44.5	32.5	46.0	33.0	47.4	33.6	48.8	34.2	50.2	34.8	51.6	35.4
14.0	36.0	30.0	37.4	30.6	38.8	31.2	40.2	31.8	41.6	32.4	43.0	33.0	44.5	33.5	45.9	34.1	47.3	34.7	48.7	35.3	50.1	35.9
15.0	34.6	30.4	36.0	31.0	37.4	31.6	38.8	32.2	40.2	32.8	41.6	33.4	43.1	33.9	44.5	34.5	45.9	35.1	47.3	35.7	48.7	36.3
16.0	33.1	30.9	34.5	31.5	35.9	32.1	37.3	32.7	38.7	33.3	40.1	33.9	41.6	34.4	43.0	35.0	44.4	35.6	45.8	36.2	47.2	36.8
17.0	31.6	31.4	33.0	32.0	34.4	32.6	35.8	33.2	37.2	33.8	38.6	34.4	40.1	34.9	41.5	35.5	42.9	36.1	44.3	36.7	45.7	37.3
18.0	30.2	31.1	31.6	32.4	33.0	33.0	34.4	33.6	35.8	34.2	37.2	34.8	38.7	35.3	40.1	35.9	41.5	36.5	42.9	37.1	44.3	37.7
19.0	28.7	32.3	30.1	32.9	31.5	33.5	32.9	34.1	34.3	34.7	35.7	35.3	37.2	35.8	38.6	36.4	40.0	37.0	41.4	37.6	42.8	38.2
20.0	27.2	32.8	28.6	33.4	30.0	34.0	31.4	34.6	32.8	35.2	34.2	35.8	35.7	36.3	37.1	36.9	38.5	37.5	39.9	38.1	41.3	38.7
21.0	25.8	33.2	27.2	33.8	28.6	34.4	30.0	35.0	31.4	35.6	32.8	36.2	34.3	36.7	35.7	37.3	37.1	37.9	38.5	38.5	39.9	39.1
22.0	24.3	33.7	25.7	34.3	27.1	34.9	28.5	35.5	29.9	36.1	31.3	36.7	32.8	37.2	34.2	37.8	35.6	38.4	37.0	39.0	38.4	39.6
23.0	22.9	34.1	24.3	34.7	25.7	35.3	27.1	35.9	28.5	36.5	29.9	37.1	31.4	37.6	32.8	38.2	34.2	38.8	35.6	39.4	37.0	40.0
24.0	21.4	34.6	22.8	35.2	24.2	35.8	25.6	36.4	27.0	37.0	28.4	37.6	29.9	38.1	31.3	38.7	32.7	39.3	34.1	39.9	35.5	40.5
25.0	20.0	35.0	21.4	35.6	22.8	36.2	24.2	36.8	25.6	37.4	27.0	38.0	28.5	38.5	29.9	39.1	31.3	39.7	32.7	40.3	34.1	40.9



in the furnace will be increased. Heating the blast to 200 or 300° C. will make a marked difference in the degree of concentration.<sup>1</sup> Experiments in substituting oil for coke have been made at Van Anda, B. C., by Kiddie<sup>2</sup> and at Tucson, Ariz., by Waters.<sup>3</sup>

**113. Chemistry.**—Detailed investigations into the chemistry of partial pyritic smelting are lacking. The blast entering through the tuyères will find the smelting zone higher and more narrowed than in a reducing fusion, and lower as well as less narrowed than in pure pyritic work. It will oxidize mainly coke and in a less degree some of the FeS that is trickling downward. Above the smelting zone the ascending gas current will consist of N, CO<sub>2</sub>, CO, SO<sub>2</sub> and some free O; the oxidizing power of the O will be greatly weakened by the presence of CO<sub>2</sub> and SO<sub>2</sub>. The O will act upon FeS; whether its oxidizing power is strong enough to have a converting effect as in the smelting zone or only a roasting effect, will be determined by the temperature and by the volume of the other gases in the current. Thus Wright<sup>4</sup> found that combustion of S ceased in an atmosphere containing 12 per cent. vol. SO<sub>2</sub>. The gas-current will be charged with S-vapor at 700° C., and this will burn at the surface of the charge. It may be noted that in most partial pyritic furnaces the volume of blast forced into the furnace is so large that the top of the charge is usually at a red heat. In other words, in order to obtain any considerable pyritic effect in the presence of coke, it is essential to have a large volume of air that unconsumed O may reach the region above the smelting zone and have there some oxidizing effect upon FeS. The overlying bed of charge is not sufficiently deep to take up most of the heat, which causes the top to become heated. The atmosphere in the furnace will have hardly any reducing power whatever. This is shown by the two gas analyses of Hermann<sup>5</sup> which showed CO<sub>2</sub> (from fuel) 8.3, CO<sub>2</sub> (from limestone) 2.6, SO<sub>2</sub> 2.5, CO 2.15, O 8.00 per cent. vol.; and CO<sub>2</sub> (from fuel) 14.1, CO<sub>2</sub> (from limestone) 3.1, SO<sub>2</sub> 3.5, CO 3.2 per cent. vol., O n.d. Furnace gases from the Copper Queen smeltery contained 10 per cent. vol. O. Dunn<sup>6</sup> gives the following analyses: SO<sub>2</sub> 1.274, SO<sub>3</sub> 0.086, CO<sub>2</sub> 6.493, H<sub>2</sub>O 3.490, As<sub>2</sub>O<sub>3</sub> 0.0091, O 10.18, N 78.13 per cent. vol.

In the descending ore-charge the changes are probably the following: There will be first a loss of hygroscopic and chemically combined H<sub>2</sub>O; then the charge will become permeated by S-vapor, which has a sulphurizing effect; farther down O, CO<sub>2</sub>, and SO<sub>2</sub> will act upon coke, the O alone upon FeS, which may be converted into Fe<sub>2</sub>SiO<sub>4</sub> or only into Fe<sub>2</sub>O, to combine later on with SiO<sub>2</sub>. As the charge reaches the smelting zone proper, fusion will take place in the same way as in the regular reducing smelting.

**114. Management and Results.**—The characteristics of the furnace are a

<sup>1</sup> Peters, *Min. Ind.*, 1908, XVII, 293.

<sup>2</sup> *Eng. Min. J.*, 1911, XCII, 434.

<sup>3</sup> *Op. cit.*, 1913, XCVI, 203.

<sup>4</sup> "Pyrite Smelting," p. 227.

<sup>5</sup> *West. Chem. and Met.*, 1905, I, 145.

<sup>6</sup> *Tr. A. I. M. E.*, 1913, XLVI.

hot top and a cool tuyère-region on account of the large volume of blast and the small amount of coke used to obtain a pyritic effect. The tuyères, therefore, have a tendency to become dark and hard, with the result that they have to be punched more or less continuously in order to get the air into the furnace; in fact, many plants have a special punching crew, which often has to use an air-hammer drill in its work.

Results of operations are given in Table 28.

**115. Calculation of Charge.**<sup>1</sup>—The calculation of a charge with the aim of forming a slag of a certain degree of silication has been given in § 102. In many smelteries it has become the custom to run the blast-furnace on a slag containing definite percentages of  $\text{SiO}_2$ ,  $\text{FeO}$ ,  $\text{CaO}$ , and other bases, as is usually the case with the typical slags made in the lead blast-furnace. As the calculation of such a charge differs from that given in § 102, it is carried through by the method with simultaneous equations, which is the most accurate.

A charge is to be calculated which is made up of ores, fluxes, and fuel given in Table 36.

TABLE 36.—ORES, FLUXES, AND COKE FOR BLAST-FURNACE CHARGE

Charge-component	$\text{SiO}_2$	$\text{Fe(Mn)O}$	$\text{Ca(Mg, Ba)O}$	$\text{Al}_2\text{O}_3$	S	Cu	Ash
First-class ore.....	50	17	1	8	17	6	.....
Coarse concentrate...	20	33	1	5	30	10	.....
Limestone.....	3	.....	50	.....	.....	.....	.....
Coke.....	.....	.....	.....	.....	.....	.....	10
Coke-ash.....	50	25	3	20	.....	.....	.....

The slag desired is:  $\text{SiO}_2$  41,  $\text{FeO}$  22,  $\text{CaO}$  23 ( $\text{Al}_2\text{O}_3$  8) per cent.; the matte shall contain Cu 45 per cent.; the coke used shall be 8 per cent. of the weight of the charge, which is to weigh 1000 lb.

A summary of the calculation is given in Table 37.

(1) MATERIALS REQUIRED TO PRODUCE 100 LB. SLAG.—Let  $x$  = lb. first-class ore,  $y$  = lb. coarse concentrate,  $z$  = lb. limestone; then  $0.08(x+y+z)$  = necessary lb. of coke which carry  $0.1 \times 0.08 (x+y+z)$  lb. coke-ash.

(2) IRON REQUIRED FOR MATTE.—The matte is to assay Cu 45 per cent.; it will contain Fe 27.8 per cent. which corresponds to  $\text{FeO}$  35.7 per cent.

The first-class ore contains Cu 6 per cent. which requires  $\text{FeO}$  4.8 per cent. for matte and leaves  $\text{FeO}$   $17 - 4.8 = 12.2$  per cent. to be slagged.

The concentrate contains Cu 10 per cent. which requires  $\text{FeO}$  7.9 per cent. for matte and leaves  $\text{FeO}$   $33 - 7.9 = 25.1$  per cent. to be slagged.

<sup>1</sup> Furman, *School Min. Quart.*, 1896, XVIII, 1.  
Barbour, *Min. Sc. Press*, 1909, XCIX, 664.  
Mostowitsch, *Metallurgie*, 1912, IX, 559.

TABLE 37.—SUMMARY OF CALCULATION OF BLAST-FURNACE-CHARGE

Charge component		SiO <sub>2</sub>		Fe(Mn)O		Ca(Mg.Ba)O		Al <sub>2</sub> O <sub>3</sub>		S		Cu	
Name	Weight	Per cent.	Weight	Per cent.	Weight	Per cent.	Weight	Per cent.	Weight	Per cent.	Weight	Per cent.	Weight
First-class ore.....	342	50	171.10	17	58.1	1	3.4	8	27.4	17	58.1	6	20.5
Coarse concentrate.....	382	20	76.4	33	126.0	1	3.8	5	19.1	30	114.6	10	38.2
Limestone.....	276	3	8.3	.....	.....	50	138.0	.....	.....	.....	.....	.....	.....
Coke-ash.....	(8)	50	4.0	25	2.0	3	0.2	20	1.6	.....	.....	.....	.....
Total.....	1000	.....	259.7	.....	186.1	.....	145.4	.....	48.1	.....	172.7	.....	58.7
Deduct for matte.....	.....	.....	.....	.....	46.6 (= 36.2Fe)	.....	.....	.....	.....	.....	35.5	.....	.....
Leaves.....	.....	.....	259.7	.....	139.5	.....	145.4	.....	48.1	.....	137.2	.....	58.7
Slag-factor 0.158.....	.....	41	.....	22	.....	23	.....	7.6	.....	.....	.....	.....	.....
Matte-factor 0.766.....	.....	.....	.....	27 Fe	.....	.....	.....	.....	.....	28	.....	45	.....

(3) ORE, FLUX, AND COKE-ASH REQUIRED TO FURNISH  $\text{SiO}_2$ ,  $\text{FeO}$ , AND  $\text{CaO}$  FOR 100 LB. SLAG.

The  $\text{SiO}_2$  in 100 lb. slag =  $0.50x + 0.20y + 0.03z + 0.50 \times 0.008 (x + y + z)$ .

The  $\text{FeO}$  in 100 lb. slag =  $0.122x + 0.251y + 0.25 \times 0.008 (x + y + z)$ .

The  $\text{CaO}$  in 100 lb. slag =  $0.01x + 0.01y + 0.50z + 0.03 \times 0.008 (x + y + z)$ .

The three simultaneous equations are

$$0.504x + 0.204y + 0.034z = 41 \quad (1)$$

$$0.124x + 0.253y + 0.002z = 22 \quad (2)$$

$$0.01024x + 0.01024y + 0.50024z = 23 \quad (3)$$

Solved, they give:  $x = 54.0$  lb. first class ore

$y = 60.3$  lb. coarse concentrate

$z = 43.7$  lb. limestone

Total = 158.0 lb. ore and flux for 100 lb. slag.

(4) REFERENCE TO 1000-LB. CHARGE.—To find the amounts of each of the charge-components required in a 1000-lb. charge, each has to be multiplied by a factor  $m$ ;  $158m = 1000$ ,  $m = 6.329$ .

This gives:  $54.0 \times 6.329 = 342$  lb. first class ore

$60.3 \times 6.329 = 382$  lb. coarse concentrate

$43.7 \times 6.329 = 276$  lb. limestone

Total = 1000 lb. charge

(5) PROOF OF CALCULATION.—From Table 37, 1000 lb. charge contains 58.7 lb. Cu which corresponds to 130.5 lb. 45-per cent. matte; this amount of matte requires 46.6 lb.  $\text{FeO}$ ; deducting 46.6 from 186.1  $\text{FeO}$  present, leaves 139.5 lb. to be slagged.

There are present in 1000 lb. charge 259.7 lb.  $\text{SiO}_2$ ; the factor for reducing this figure to 41 is 259.7  $n = 41$ ,  $n = 0.158$ . Multiplying the totals of  $\text{SiO}_2$ ,  $\text{FeO}$ ,  $\text{CaO}$ , and  $\text{Al}_2\text{O}_3$  of Table 37 entering the slag, by this factor gives:  $\text{SiO}_2$  41,  $\text{FeO}$  22,  $\text{CaO}$  23,  $\text{Al}_2\text{O}_3$  7.6, the desired ratio of the slag-components.

(6) PYRITIC EFFECT.—The 130.5 lb. matte produced from 1000 lb. charge contain  $130.5 \times 27.2 = 35.5$  lb. S. There are present 172.7 lb. S, hence  $172.7 - 35.5 = 137.2$  lb. = 79.4 per cent. have to be burned off.

#### 116. Thermal Balance Sheets of Some Partial Pyritic Smelting Operations.

—Details of two thermal balance sheets are given, representing sulphide-ore treatment and matte-concentration as carried out by the Ducktown Sulphur, Copper, and Iron Co., Isabella, Tenn., the data having been furnished by Mr. W. F. Lamareaux. There is added for sake of comparison a condensed balance sheet of the partial pyritic smelting of ore by the Washoe plant of the Anaconda Copper Mining Co., furnished by Mr. E. P. Mathewson.

These heat balances furnish an insight into the manner in which the heat has been generated, in which it has been utilized by chemical action and fusion, and in which it has been lost by radiation, convection, escaping gases, etc.

Before the thermal balance sheet can be cast, it is essential to prepare a theoretical balance sheet of the materials.

**I. PARTIAL PYRITIC ORE SMELTING.**—The basis of calculation chosen is that of 1000 kg. charge with 50 kg. coke. The ultimate analysis of the ore is, Cu 2.55, Fe 26.8, S 17.27,  $\text{SiO}_2$  28.38, CaO 8.11, MgO 3.83,  $\text{Al}_2\text{O}_3$  3.39, Zn 2.93, O,  $\text{CO}_2$ , etc., 6.74 per cent. The rational analysis calculated from the ultimate and the known character of the mineral constituents shows that the charge is composed of: chalcopyrite ( $\text{CuFeS}_2$ ) 7.4, sphalerite ( $\text{ZnS}$ ) 4.4, pyrrhotite ( $\text{Fe}_7\text{S}_8$ ) 33.5, biotite ( $\text{Al Fe}_2\text{Si}_4\text{O}_{16}$ ) 12.2, actinolite [ $\text{Ca}(\text{MgFe})_3\text{Si}_4\text{O}_{12}$ ] 17.1, calcite ( $\text{CaCO}_3$ ) 10.4, quartz ( $\text{SiO}_2$ ) 14.1, Undetermined 0.9, Total 100 per cent. The matte produced in the smelting had the following composition: Cu 16.0, Fe 49.8, S 24.9,  $\text{SiO}_2$  0.8, CaO 0.3, Insol. 2.1, Undetermined 6.1 per cent.

In the theoretical balance-sheet of materials given in Table 38, it has been assumed, (1) that all the Cu has entered the matte, and that any Cu found in the slag is present as a matte pellet; (2) that the weight of the matte may be calculated from its analysis and the weight of the Cu in the charge, only Cu, Fe, Zn, and S being assigned to matte, the rest to slag; (3) that of the Zn not present in the matte, one-half has entered the slag as ZnS, the other has been carried off as ZnO in the gases. Of the materials entering the furnace and placed on the debit-side, there remain to be determined the O, or air necessary for oxidation of constituents, and the accompanying moisture.

The O required by the charge is:

(1)  $\text{CuFeS}_2$ .—The whole is assumed to enter the matte unchanged.

(2) Fe to  $\text{FeO}$ .—Of the 202.0 kg. Fe furnished by 335.0 kg.  $\text{Fe}_7\text{S}_8$ , 57.1 kg. enter the matte and 144.9 the slag; all the Fe of the coke-ash, *i.e.*, 1.1 kg., enters the slag, or  $144.9 + 1.1 = 146$  kg. Fe enter the slag as  $\text{FeO}$ . These require ( $\text{Fe}:\text{O} = 56:16 = 146:21$ ). . . . . 41.7 kg. O.

(3) S to  $\text{SO}_2$ .—Of the 14.5 kg. S furnished by 44 kg. ZnS, 6.3 kg. are oxidized; of the 133 kg. S furnished by 335 kg.  $\text{Fe}_7\text{S}_8$ , 120.7 kg. are oxidized; all the S in the coke, 0.8 kg., is oxidized; or  $6.3 + 120.7 + 0.8 = 127.8$  kg. S are oxidized. These require ( $\text{S}:\text{O}_2 = 32:32 = 127.8:32$ ). . . . . 127.8 kg. O.

(4) C to  $\text{CO}_2$ .<sup>1</sup>—All of the 42.0 kg. C of the coke are oxidized; they require therefore ( $\text{C}:\text{O}_2 = 12:32 = 42.0:112$ ). . . . . 112.0 kg. O.

(5) Zn to ZnO. —Of the 29.5 kg. Zn furnished by 44 kg. ZnS, 13.0 kg. are oxidized. They require ( $\text{Zn}:\text{O} = 65:16 = 13.0:3.2$ ). . . . . 3.2 kg. O.

(6) The total O theoretically required is therefore  $41.7 + 127.8 + 112.0 + 3.2$ . . . . . 284.7 kg. O. and the accompanying N, 953, corresponding to 756.4 cu. m.

(7) The volume of gases is 127.8 kg. S + 127.8 kg. O = 255.6 kg.  $\text{SO}_2 = 88.7$  cu. m.; 42.0 kg. C + 112.0 kg. O = 154 kg.  $\text{CO}_2$  from coke, and 45.8 kg.  $\text{CO}_2$  from limestone, or 199.8 kg.  $\text{CO}_2 = 101$  cu. m. This gives as total volume  $756.4 \text{ N} + 88.7 \text{ SO}_2 + 101.0 \text{ CO}_2 = 946.1$  cu. m. But the waste gas carries 8 vol. excess O which corresponds to 40 vol. excess air. The above 946.1 cu. m. form therefore only 60 per cent. of the true volume, which is 1577 cu. m. at  $0^\circ\text{C}$ . and 760 mm. Hg.

<sup>1</sup> The gas contains free O, hence no CO can form.

TABLE 38.—THEORETICAL BALANCE SHEET OF MATERIALS OF ONE ORE CHARGE OF 1000 KG.

Debit							Credit		
	Mineral	Per cent.	Wt., kg.	Constituent	Per cent.	Wt., kg.	Matte, kg.	Slag, kg.	Gas, kg.
Ore Charge, 1000 kg.	CuFeS <sub>2</sub>	7.4	74.0	.....	.....	.....	.....	.....	.....
	.....	.....	.....	Cu	34.6	25.6	25.6	.....	.....
	.....	.....	.....	Fe	30.5	22.6	22.6	.....	.....
	.....	.....	.....	S	34.9	25.8	25.8	.....	.....
	ZnS	4.4	44.0	.....	.....	.....	.....	.....	.....
	.....	.....	.....	Zn	67.0	29.5	3.4	13.1	13.0
	.....	.....	.....	S	33.0	14.5	1.7	6.5	6.3
	Fe <sub>7</sub> S <sub>8</sub>	33.5	335.0	.....	.....	.....	.....	.....	.....
	.....	.....	.....	Fe	60.4	202.0	57.1	144.9	.....
	.....	.....	.....	S	39.6	133.0	12.3	.....	120.7
	(AlFe <sub>7</sub> ) <sub>2</sub> Si <sub>4</sub> O <sub>18</sub>	12.2	122.0	.....	.....	.....	.....	.....	.....
	.....	.....	.....	Al <sub>2</sub> O <sub>3</sub>	27.8	33.9	.....	33.9	.....
	.....	.....	.....	SiO <sub>2</sub>	39.4	48.1	.....	48.1	.....
	.....	.....	.....	FeO	32.8	40.0	.....	40.0	.....
	Ca(MgFe) <sub>2</sub> Si <sub>4</sub> O <sub>12</sub>	17.1	171.0	.....	.....	.....	.....	.....	.....
	.....	.....	.....	CaO	13.4	22.9	.....	22.9	.....
	.....	.....	.....	MgO	22.4	38.2	.....	38.2	.....
	.....	.....	.....	FeO	9.0	15.4	.....	15.4	.....
	.....	.....	.....	SiO <sub>2</sub>	55.2	94.5	.....	94.5	.....
	CaCO <sub>3</sub>	10.4	104.0	.....	.....	.....	.....	.....	.....
	.....	.....	.....	CaO	56.0	58.2	.....	58.2	.....
	.....	.....	.....	CO <sub>2</sub>	44.0	45.8	.....	.....	45.8
	SiO <sub>2</sub>	14.1	.....	.....	.....	141.0	.....	141.0	.....
	X	0.9	.....	.....	.....	9.0	.....	9.0	.....
Coke, 50 kg.	.....	.....	.....	Fe	2.3	1.1	.....	1.1	.....
	.....	.....	.....	S	1.6	0.8	.....	.....	0.8
	.....	.....	.....	SiO <sub>2</sub>	8.4	4.2	.....	4.2	.....
	.....	.....	.....	Al <sub>2</sub> O <sub>3</sub>	3.6	1.8	.....	1.8	.....
	.....	.....	.....	C	83.9	42.0	.....	.....	42.0
	.....	.....	.....	X	0.2	0.1	.....	.....	0.1
Blast (dry) 2079 kg.	.....	.....	.....	O	23.0	478.0	.....	41.4	436.6
	.....	.....	.....	N	77.0	1601.0	.....	.....	1601.0
Water, 31.7 kg.	In charge.....	.....	.....	.....	.....	10.0	.....	.....	10.0
	In blast.....	.....	.....	.....	.....	21.7	.....	.....	21.7
Totals...	.....	.....	.....	.....	.....	3160.7	148.5	714.2	2298.0

(8) VOLUME OF BLAST.—The volume of O necessary to form  $\text{CO}_2$  and  $\text{SO}_2$  is 189.7 cu. m., that to form  $\text{FeO}$  and  $\text{ZnO}$ , 31.0 cu. m.; the accompanying N and excess air give 1387.3 cu. m.; hence the volume of blast at  $0^\circ \text{C}$ . and 760 mm. Hg is 1608.0 cu. m. = 2079 kg.

(9) MOISTURE IN CHARGE AND BLAST.—The charge has 1 per cent or 10 kg.  $\text{H}_2\text{O}$ , the blast 13.5 g. per cubic meter, or  $0.1608 \times 13.5 = 2.17$  kg., all of which passes off with the gases.

In casting the thermal balance for a charge of 1000 kg. ore and flux, and 50 kg. coke, given in Table 39, the in-coming heat is placed in the debit column, the out-going in that of the credit. The details of the calculation are as follows:

(A) Burning C to  $\text{CO}_2$ , 8100 Cal. per kg. C:

$$42 \times 8100 = 340,200 \text{ Cal.}$$

(B) Burning S to  $\text{SO}_2$ , 2164 Cal. per kg. S:

$$(6.3 \text{ kg. S from ZnS}) + (120.7 \text{ kg. S from Fe}_7\text{S}_8) + (0.8 \text{ kg. S from coke}) = 127.8 \text{ kg.}$$

$$127.8 \times 2164 = 276,560 \text{ Cal.}$$

TABLE 39.—THERMAL BALANCE FOR ONE ORE CHARGE OF 1000 KG.

Debit			Credit		
	Kilogram calories	Per cent. of total		Kilogram calories	Per cent. of total
(A) Burning C to $\text{CO}_2$ .....	340,200	39.2	(I) Reduction of $\text{CaCO}_3$ .....	46,991	5.4
(B) Burning S to $\text{SO}_2$ .....	276,560	31.9	(J) Reduction of $\text{FeS}$ .....	62,104	7.1
(C) Burning Fe to $\text{FeO}$ .....	169,968	19.5	(K) Reduction of $\text{ZnS}$ .....	8,600	1.0
(D) Burning Zn to $\text{ZnO}$ .....	16,965	2.0	(L) Heat in matte.....	33,413	3.9
(E) Formation of $2\text{FeO} \cdot \text{SiO}_2$ .....	31,816	3.6	(M) Heat in slag.....	232,115	26.7
(F) Formation of $\text{CaO} \cdot \text{SiO}_2$ .....	18,554	2.1	(N) Heat in gas.....	354,633	40.8
(G) Sensible heat in charge.....	5,250	0.6	(O) Radiation and conduction (by difference).	131,201	15.1
(H) Sensible heat in blast.....	9,744	1.1			
	869,057	100.0		869,057	100.0

(C) Burning Fe to  $\text{FeO}$ , 1173 Cal. per kg. Fe:

The 144.9 kg. Fe from  $\text{Fe}_7\text{S}_8$  entering the slag are oxidized to  $\text{FeO}$ .

$$144.9 \times 1173 = 169,968 \text{ Cal.}$$

(D) Burning Zn to  $\text{ZnO}$ , 1305 Cal. per kg. Zn:

The 13.0 kg. Zn not entering matte and slag as  $\text{ZnS}$  are oxidized to  $\text{ZnO}$ .

$$13.0 \times 1305 = 16,965 \text{ Cal.}$$

(E) Formation of  $2\text{FeO} \cdot \text{SiO}_2$ , 154 Cal. per kg.  $\text{FeO}$ :

The 33.9 kg.  $\text{Al}_2\text{O}_3$  in  $(\text{AlFe})_2\text{Si}_4\text{O}_{16}$  are assumed to enter the slag as  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ . This silicate contains 39.9 kg.  $\text{SiO}_2$ , leaving  $48.1 - 35.9 = 8.2$  kg.  $\text{SiO}_2$  which are assumed to be combined with  $\text{FeO}$  as  $2\text{FeO} \cdot \text{SiO}_2$ .

The 8.2 kg.  $\text{SiO}_2$  require 19.7 kg.  $\text{FeO}$ , leaving  $40.0 - 19.7 = 20.3$  kg.

FeO uncombined with  $\text{SiO}_2$ . The 144.9 kg. Fe from (C) correspond to 186.3 kg. FeO; the total  $\text{FeO} = 20.3 + 186.3 = 206.6 \text{ kg.} = 154 \times 206.6 = 31,816 \text{ Cal.}$

(F) Formation of  $\text{CaO.SiO}_2$ , 318.8 Cal. per kg. CaO.

The 104.0 kg.  $\text{CaCO}_3$  furnish 58.2 kg. CaO.

$$58.2 \times 318.8 = 18,554 \text{ Cal.}$$

(G) Sensible Heat in charge at  $20^\circ \text{C.}$ , spec. heat = 0.25 app.

$$1050 \times 0.25 \times 20 = 5250 \text{ Cal.}$$

(H) Sensible Heat in Blast at  $20^\circ \text{C.}$ , spec. heat = 0.303 app., volume of blast = 1,608 cu. m.

$$1068 \times 0.303 \times 20 = 9744 \text{ Cal.}$$

(I) Dissociation of  $\text{CaCO}_3$ , 1026 Cal. per kg.  $\text{CO}_2$ .

$$45.8 \times 1026 = 4,6991 \text{ Cal.}$$

(J) Dissociation of  $\text{Fe}_7\text{S}_8$ , 428.6 Cal. per kg. Fe.

The Fe entering the slag from  $\text{Fe}_7\text{S}_8$  has to be set free before it is oxidized.

$$144.9 \times 428.6 = 62,104 \text{ Cal.}$$

(K) Dissociation of  $\text{ZnS}$ , 661.5 Cal. per kg. Zn.

The Zn entering the gas from  $\text{ZnS}$  has to be set free before it is oxidized.

$$13.0 \times 661.5 = 8600 \text{ Cal.}$$

(L) Heat in Matte, 225 Cal. per kg. app.

$$148.5 \times 225 = 33,413 \text{ Cal.}$$

(M) Heat in Slag, 325 Cal. per kg. app.

$$714.2 \times 325 = 232,115 \text{ Cal.}$$

(N) Heat in Gas, temperature  $600^\circ \text{C.}$

Gas analysis =  $\text{SO}_2$  5.4,  $\text{CO}_2$  6.3, O 8.0, N 80.3 per cent. vol. Volume of gas, at  $0^\circ \text{C}$  and 760 mm. Hg, 1577, cu. m. divides as follows:  $\text{SO}_2 = 1577 \times 0.054 = 85.2 \text{ cu. m.}$ ;  $\text{CO}_2 = 1577 \times 0.063 = 99.4 \text{ cu. m.}$ ; N and O =  $1577 \times 0.883 = 1392.4 \text{ cu. m.}$  The mean spec. heats between zero and  $600^\circ \text{C.}$  are  $\text{SO}_2$ , 0.54;  $\text{CO}_2$ , 0.502; O and N, 0.3192, hence the total heat in the gases,  $(85.2 \times 0.54 + 99.4 \times 0.502 + 1392.4 \times 0.3192) \times 600 = 324,217 \text{ Cal.}$

There has to be added the heat contained in 31.7 kg.  $\text{H}_2\text{O}$ . and 13.0 kg.  $\text{ZnO}$ . The heat of evaporation of  $\text{H}_2\text{O}$  at  $0^\circ \text{C.}$  = 606.5 Cal. per kg., hence  $31.7 \times 606.5 = 19,226 \text{ Cal.}$ ; the mean spec. heat of the gas between zero and  $600^\circ \text{C.}$  = 0.531, hence  $31.7 \times 0.531 \times 600 = 10,098 \text{ Cal.}$ , or the total heat in the water vapor =  $19,226 + 10,098 = 29,324 \text{ Cal.}$  The mean spec. heat of  $\text{ZnO}$  between zero and  $600^\circ \text{C.}$  = 0.14, hence  $13.0 \times 0.14 \times 600 = 1,092 \text{ Cal.}$  The total heat in the gas is therefore  $324,217 + 29,324 + 1,092 = 354,633 \text{ Cal.}$

II. PARTIAL PYRITIC MATTE CONCENTRATION.—The mode of procedure in calculating a thermal balance was exactly the same as the one followed in the first case with ore-smelting. The calculation is based upon the concentration of 1000 kg. matte (Cu 16.0, Fe 49.8, Zn 2.1, S 24.9, Undet. 7.2 per cent.) with 293 kg. quartz and 50 kg. coke to converter-matte containing Cu 51.1,



Fe 22.2, S 23.3, SiO<sub>2</sub> 0.21, Zn 0.8, Undet. 2.5 per cent. Table 40 gives the theoretical balance sheet of materials of one charge of 1000 kg. matte, and Table 41 the thermal balance sheet.

TABLE 40.—THEORETICAL BALANCE SHEET OF MATERIALS OF ONE CHARGE OF 1000 KG.

Debit			Credit		
	Per cent.	Weight, kg.	Matte, kg.	Slag, kg.	Gas, kg.
Matte, 1000 kg.					
Cu.....	16.0	160.0	160.0		
Fe.....	49.8	498.0	69.5	428.5	
Zn.....	2.1	21.0	2.5	9.2	9.3
S.....	24.9	249.0	73.6	4.6	170.8
X.....	7.2	72.0		72.0	
Quartz, 293 kg..					
SiO <sub>2</sub> .....	100.0	293.0		293.0	
Coke, 50 kg.:					
C.....	83.9	41.9			41.9
Fe.....	2.3	1.2		1.2	
S.....	1.6	0.8			0.8
SiO <sub>2</sub> .....	8.4	4.2		4.2	
X.....	3.8	1.9			1.9
Blast, 2874 kg.:					
N.....	77.0	2213.0			2213.0
O.....	23.0	661.0		122.8	538.2
Moisture, 40 kg.:					
In matte.....		10.0			
In blast.....		30.0			
Total.....		4257.0	305.6	935.5	3015.9

TABLE 41.—THERMAL BALANCE FOR ONE CHARGE OF 1000 KG. MATTE.

Debit			Credit		
Item	Kilogram calories	Per cent. of total	Item	Kilogram calories	Per cent. of total
Burning C to CO <sub>2</sub> .....	339,390	26.2	Dissociation, FeS.....	183,655	14.2
Burning S to SO <sub>2</sub> .....	371,342	28.8	Dissociation, ZnS.....	6,152	0.5
Burning Fe to FeO.....	504,038	38.9	Heat in matte.....	68,760	5.3
Burning Zn to ZnO.....	12,137	0.9	Heat in slag.....	304,038	23.5
Formation of slag.....	44,075	3.4	Heat in gas.....	471,418	36.4
Heat in charge.....	6,715	0.5	Radiation, conduction (diff.)....	261,090	20.1
Heat in blast.....	17,416	1.3			
	1,295,113	100.0		1,295,113	100.0

III. PARTIAL PYRITIC ORE SMELTING AT WASHOE SMELTERY, ANACONDA COPPER MINING CO.—The thermal balance sheet given in Table 42 is one figured to a basis of 1000 kg. charge from the official sheet furnished by Mr. E. P. Mathewson.

TABLE 42.—THERMAL BALANCE SHEET FOR ONE ORE CHARGE OF 1000 KG. ANACONDA, MONT.

Debit			Credit		
Item	Kilogram calories	Per cent. of total	Item	Kilogram calories	Per cent. of total
Burning coke.....	569,948	64.5	Dissociation, $\text{CaCO}_3$ .....	121,710	13.8
Burning S.....	138,952	15.7	Dissociation, $\text{FeS}$ .....	7,086	0.8
Burning Fe.....	80,461	9.1	Dissociation, $\text{MgCO}_3$ .....	3,804	0.4
Burning Zn.....	8,881	1.0	Heat in gases.....	459,953	52.0
Formation of slag.....	77,158	8.7	Heat in flue dust.....	13,449	1.5
Brought in by blast.....	8,599	1.0	Heat in matte.....	30,311	3.4
			Heat in slag.....	200,773	22.7
			Heat in cooling water.....	14,576	1.7
			Loss by radiation, (diff.).....	32,337	3.7
	883,999	100.0			
				883,999	100.0

One striking feature of the two theoretical balance sheets of materials, given in Tables 38 and 40, is that the weight of the gases produced greatly exceeds that of the charge fed.

Of the three thermal balances, the data of Ducktown, Tables 39 and 41, show that more heat is derived here from oxidation of Fe and S, than at Anaconda, Table 42; also that their losses of heat by radiation and conduction is very much larger. The three thermal tables show, that the largest part of the heat generated in the furnace is carried off by the gases, and that the slag follows next in order.

**117. General Smelting Operations.**—These are the blowing-in, the regular work on the feed- and furnace-floors, and the blowing-out.

In starting, it is advisable to make up a charge which will run easily and furnish a matte with Cu 30–35 per cent., as this runs hot and heats up the crucible and the fore-hearth. When the furnace runs well on a slag that is easily formed and on a high percentage of coke, the change is made to the kind of charge it is the intention to run, be the process reducing, pyritic, or partial pyritic smelting. The following gives in detail two modern examples of blowing-in furnaces in partial pyritic smelting.

At the smeltery of the Tennessee Copper Co., Geo. A. Guess<sup>1</sup> used to proceed as follows: A new crucible is warmed for 24 hr. by burning wood. When warm, it is cleaned out, and light wood (scrap boards, broken lumber), charged to reach to the tuyères. With an old furnace the bottom is only 6–8

<sup>1</sup> Private Communication, August, 1912.

in. below the tuyères, hence much less wood is required than when the crucible is new. The wood is ignited from end to end with oil-soaked waste; no blast is used; the necessary air enters through the tuyère openings. When the wood burns freely, more is charged to reach well above the tuyères; care is taken that the wood lie flat, *i.e.*, that there shall be no pieces of cord wood pointing upward. If the wood is dry, no blast is needed, but if wet, some air is turned on which is made to enter through alternate tuyères. As soon as the bed of wood is burning freely all over, coke is charged, about 40 lb. per square foot of hearth area. Some blast is now necessary; as soon as the coke appears to be well ignited all over, the plugged tuyères are uncovered, and air with a pressure of about 2 oz. turned on. The breast of the furnace has not been closed; an open breast assists in blowing out ashes, etc.

When the coke is red on top, the furnace receives its charges in quick succession. The blowing-in charges, six in number, differ from the normal, in that they are made less siliceous and carry 50 per cent. more coke. As soon as the first charge has been fed, the blast-pressure is raised to about 8 oz. Bits of charcoal, coke, etc., are blown with the flame out of the breast, and the bottom is cleaned and heated. This continues until fluid slag with some matte has trapped the blast, which happens in from 30 to 40 min. after the first blowing-in charge has been given. Matte and slag now overflow into the preheated settler; the blast is gradually increased until, in about 10 hr. after the first blowing-in charge, full blast has been put on.

It will be noticed that no slag is used in blowing-in an ore-furnace; with a matte-concentrating furnace some slag is used at first, although it is not absolutely necessary.

At the Garfield smelter<sup>1</sup> A. E. Wells<sup>1</sup> used the following procedure: The bottom of the crucible is lined with about 12 in. of silica well tamped down. In order to dry it, a slow wood fire is kept going for 18 hr., and then a brisk fire 6 hr. A new settler is dried and warmed with a wood fire for 48 hr. When crucible and settler are warm, the furnace is filled with scrap wood to reach about 2 ft. above the tuyères, the wood is kindled and the furnace filled; the wood burns with natural draft while the blowing-in charges are dropped. On top of the wood are spread 6000 lb. coke followed by nine blowing-in charges of 6000 lb., consisting of sulphide ore ( $>\frac{3}{4}$  in.) 2000 lb., converter slag (fist-size) 3000 lb., limestone 1000 lb., coke 600 lb. The blowing-in charges make a matte with Cu 25 per cent. and a slag with  $\text{SiO}_2$  36, FeO 45, CaO 14 per cent. As soon as the blowing-in charges have been fed, blast is put on (15,000 cu. ft. per minute, engine displacement), which gives at the tuyères a pressure of 20-25 oz. A flame is allowed to escape for a few minutes through the connecting-hole in the breast-block to blow out half-burnt wood and coke which might obstruct the passage of the slag. When slag begins to collect around the connection-hole, this is loosely plugged with a clayey brasque, and a 2-in. bar pushed through the latter. In about 15 min. the slag has risen sufficiently to trap the blast, the bar is pulled out, and the slag-

<sup>1</sup>Private Communication, August, 1912.

matte allowed to overflow into the settler. The blowing-in charges are gradually replaced by ore-charges; one of the former is followed by two of the latter; and the furnace is run for 2 hr. on this mixture. The charge-column is now raised to its normal height, and the blast is increased to 21,000 cu. ft. air per minute, which raises the pressure to about 35 oz. The regular work of the furnace is given in Table 28.

The operations such as feeding of charge (§ 93) and tapping of matte and handling of slag (§ 94) have already been discussed. The work on the feed-floor and furnace-floor has been indicated in §§ 93 and 94. In blowing-out, slag-charges are substituted for ore-charges until most of the ore-charge has been smelted. Charging is stopped, the charge slowly sinks, the volume of blast admitted is lowered. When the charge has sunk to about the lower tier of jackets, the blast is stopped, the tuyère valves are closed, the furnace is tapped clean, the breast-jacket is removed, and the material remaining in the furnace raked out. When the flow of slag ceases, the contents of the fore-hearth are tapped.

## PRODUCTS

**118. Products of the Blast-furnace.**—The regular products are matte, speise, flue-dust, and gases; the irregular products, wall accretions, hearth accretions, furnace-drawings, and refuse.

**119. Matte.**<sup>1</sup>—In table 43 are given analyses of mattes with increasing contents of Cu selected from a collection published by Keller.<sup>2</sup> The leading constituents of this intermediary product are Cu, Fe, and S; the other compo-

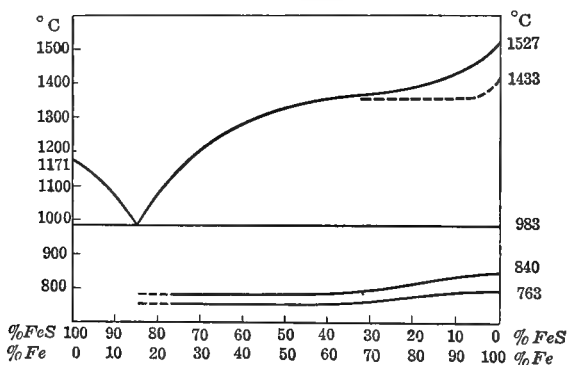


FIG. 231.—Alloy series FeS-Fe.

nents, such as Ni, Co, Zn, Pb, Bi, Sb, As, Se, Te, Ag, Au, etc., are of minor import. There will be considered the relations of Cu-Fe, Cu-Cu<sub>2</sub>S, Fe-FeS and Cu<sub>2</sub>S-FeS.

The metals Cu and Fe (p. 16) form solid solutions within a range of 96.5 per cent. Fe+3.5 per cent. Cu and 97 per cent. Cu+3 per cent. Fe.

<sup>1</sup> In England the word "Regulus" is used synonymously.

<sup>2</sup> *Min. Ind.*, 1900, IX, 243; see also Channing in Rickard's "Pyrite Smelting," p. 263.

TABLE 43.—ANALYSES OF COPPER MATTES

Source	Cu per cent.	S per cent.	Fe per cent.	Fe <sub>2</sub> O <sub>4</sub> per cent.	Ni per cent.	Co per cent.	Zn per cent.	Pb per cent.
Elizabeth M. Co., Vt.....	21.36	22.95	41.03	10.44	0.0020	0.1984	0.24	0.0226
Parrot, reverb. furn.....	36.15	23.88	24.97	8.51				
Le Roi Mine, B. C.....	49.02	22.78	23.86		0.0383	0.0332	0.09	0.0920
Ducktown, Tenn.....	49.17	19.45	22.79		0.0436	0.0222	0.77	0.1294
B. & M. Co., reverb. furn...	49.34		22.44					0.0738
Jerome, Ariz.....	55.00	23.96	13.85	2.58			1.24	3.0250
Silver City, N. M.....	53.73	23.17	19.49		0.0354	0.0498	0.26	0.0022
Copper Queen, blast-furn...	54.89	23.36	20.25		0.0341	0.0240	0.34	0.1178
Mountain Copper Co., Cal...	57.83	22.47	15.28		0.0050		2.09	0.0719
Anaconda, reverb. furn.....	60.76	23.25	11.43	1.13	0.0076	0.0034	2.41	0.5900
B. & M. Co., blast-furn.....	61.42		14.50					0.0370
Santa Rosalia, Mexico.....	61.52	22.52	13.68		0.0645	0.4140	0.2333	0.0270

TABLE 43.—ANALYSES OF COPPER MATTES—(Continued)

Source	Bi per cent.	Sb per cent.	As per cent.	Te per cent.	Se per cent.	Ag oz. per ton	Au oz. per ton
Elizabeth M. Co., Vt.....	0.0	0.0	0.0041	0.0	0.0082	2.4	0.0
Parrot, reverb. furn.....							
Le Roi Mine, B. C.....	0.0008	0.0348	0.0434	0.0063	0.0	26.0	10.72
Ducktown, Tenn.....	0.0	0.0206	0.0	0.0	0.0	5.9	0.04
B. & M. Co., reverb. furn.....	0.0337	0.1010	0.0480	0.0021		14.6	0.05
Jerome, Ariz.....	0.0174	0.2693	0.0914	0.0474	0.1172	127.0	2.28
Silver City, N. M.....	0.0	0.0032	0.0	Trace		1.2	Trace
Copper Queen, blast-furn.....	0.0044	0.0232	0.0171	0.0088	0.0113	6.0	0.10
Mountain Copper Co., Cal. N.....	0.0014	0.0143	0.0130	0.0060		13.4	0.51
Anaconda, reverb. furn.....	0.0420	0.0790	0.0450	0.0112	0.0038	60.4	0.30
B. & M. Co., blast-furn.....	0.0049	0.1330	0.1280	0.0042		18.2	0.05
Santa Rosalia, Mexico.....	0.0008	0.0032	0.0013	0.0	0.0	2.2	Trace

The saturation point of  $\text{Cu}_2\text{S}$  for Cu (p. 21) is 15 per cent.; and the eutectic  $\text{Cu-Cu}_2\text{S}$  contains 3.8 per cent.  $\text{Cu}_2\text{S}+96.2$  per cent. Cu.

The freezing-point curve for  $\text{FeS-Fe}$  has been investigated by Tammann-Treitschke<sup>1</sup> and Friedrich.<sup>2</sup> According to the diagram of Friedrich, Fig. 231, the two components form an eutectic mixture of 15 per cent. Fe and 85 per cent  $\text{FeS}$  solidifying at  $983^\circ\text{C}$ .; Fe can hold in solid solution less than 3 per cent  $\text{FeS}$  and  $\text{FeS}$  less than 1 per cent. Fe.

The constitution of  $\text{Cu}_2\text{S-FeS}$  has been traced through freezing-point curves by Röntgen,<sup>3</sup> Hofman-Cayple-Harrington,<sup>4</sup> Baykoff-Troutneff,<sup>5</sup> and Bornemann-Schreyer,<sup>6</sup> and through other methods by Münster,<sup>7</sup> Bolles,<sup>8</sup> Gibb-Philp<sup>9</sup>

<sup>1</sup> *Zt. anorg. Chem.*, 1906, XLIX, 320; *Metallurgie*, 1907, IV, 54.

<sup>2</sup> *Metallurgie*, 1910, VII, 257.

<sup>3</sup> *Metallurgie*, 1906, III, 479.

<sup>4</sup> *Tr. A. I. M. E.*, 1908, XXXVIII, 424.

<sup>5</sup> *Rev. Mét.*, 1909, VI, 518.

<sup>6</sup> *Metallurgie*, 1909, VI, 619.

<sup>7</sup> *Berg. Hüttenm. Z.*, 1877, XXXVI, 195, 210, 219.

<sup>8</sup> *Tr. A. I. M. E.*, 1905, XXXV, 666.

<sup>9</sup> *Op. cit.*, 1906, XXXVI, 665.

and Fulton-Goodner.<sup>1</sup> An eutectic mixture found by some is denied by others, although it can be seen clearly in copper matte; similar disagreements exist as regards chemical compounds and solid solutions. The question requires further investigation.

In plotting the accepted relations between Cu, Fe, and S in a tri-axial diagram, as was done by Baikoff-Troutneff,<sup>2</sup> but substituting the data of Friedrich for those of Tammann-Treitschke, Fig. 232 is obtained. This gives four fields:

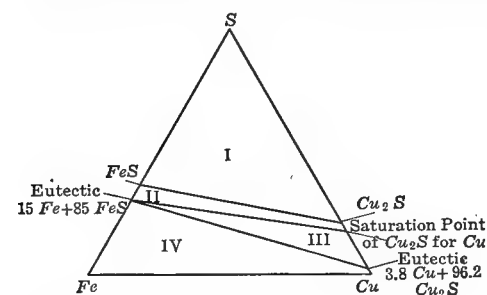


FIG. 232.—Triaxial diagram of copper-iron matte.

above their melting-points; field II the stable FeS-Cu<sub>2</sub>S mixtures forming pure matte; field III the region in which there is in the liquid state a stratification of components belonging to II and IV; field IV a matte with large amounts of solid solution of Cu and Fe. The connecting lines are drawn straight, because there are as yet no data to show their accurate positions between the end-

points. The smallness of field II shows how likely ordinary mattes are to contain metallics in which either Fe or Cu prevails.

The presence of Fe<sub>3</sub>O<sub>4</sub> to an extent of 10 per cent. in low-grade, and especially in pyritic matte,<sup>3</sup> which causes much trouble in the settler, is due to Fe<sub>3</sub>O<sub>4</sub> in the charge, or to imperfect reduction of Fe<sub>2</sub>O<sub>3</sub>; it may be caused also by oxidation of the Fe in the matte, but not by that of FeS, as in normal pyritic operation this is presupposed to be oxidized to FeO and directly combined with SiO<sub>2</sub>. In abnormal pyritic work, however, it may be formed, if, *e.g.*, there is a lack of SiO<sub>2</sub>.<sup>4</sup> As Fe<sub>3</sub>O<sub>4</sub>, with a specific gravity of 5.0 to 5.2, forms more readily with a low- than a high-grade matte, and as the specific gravity of matte increases with the Cu-content (Cu 13.62 per cent., spec. gr. 4.8; Cu 43.00, spec. gr. 5.18; Cu 60.22, spec. gr. 5.42; Cu 80.00, spec. gr. 5.55) Fe<sub>3</sub>O<sub>4</sub> will enter low-grade matte and float on high-grade matte, and thence will be taken up in part by slag and carry Au into it. Thus at Blagodatny, Ural,<sup>5</sup> with a matte of SiO<sub>2</sub> 1.2, Cu<sub>2</sub>S 17.2, FeS 61.7, PbS 6.7, Fe<sub>3</sub>O<sub>4</sub> 12.4, As, Sb, Bi 0.6 per cent., Au 6.23 oz. and Ag 66.4 oz. per ton, the slag (SiO<sub>2</sub> 45.2, FeO 28.5, CaO 22.2, N.D. 4.1) assayed

<sup>1</sup> *Op. cit.*, 1908, XXXIX, 584.

<sup>2</sup> *Loc. cit.*

<sup>3</sup> Keller, *Eng. Min. J.*, 1895, LX, 465.

Larison, *op. cit.*, 1909, LXXXVII, 1195.

Rizo-Patron, *op. cit.*, 1909, LXXXVIII, 367.

Shelby, *loc. cit.*, p. 742.

Keller, *Min. Ind.*, 1900, IX, 243.

Gibb-Philp, *Tr. A. I. M. E.*, 1906, XXXVI, 671, 1907, XXXVIII, 913.

Keller, *op. cit.*, 1906, XXXVI, 837.

<sup>4</sup> See page 199.

<sup>5</sup> Private Communication by F. W. Draper, Nov., 1908.

Au 0.03 oz. and Ag 0.59 oz. per ton., while in the absence of  $\text{Fe}_3\text{O}_4$  the slag ran Au 0.003–0.013 oz. and Ag 0.50–0.75 oz. per ton. The silver content in the slag did not appear to be affected by  $\text{Fe}_3\text{O}_4$ ; it varied directly with the assay of the matte whether  $\text{Fe}_3\text{O}_4$  was present or not.

Finely divided Cu,<sup>1</sup> so-called "moss-copper," is of frequent occurrence in matte assaying from about 30 to about 60 per cent. Cu. Fulton-Goodner<sup>2</sup> noticed it in 10-per cent. Cu-matte. It has its origin in the insolubility of Cu in  $\text{Cu}_2\text{S}$  in the solid state (§ 21). Fulton-Goodner call attention to the fact that the Cu separates from solid matte when this is relatively cool, but still too hot to be held in the hand. They attribute the separation at this low temperature tentatively to the dimorphic point of  $\text{Cu}_2\text{S}$ , which occurs at  $103^\circ\text{C}$ . The cracking vertically of conical or hemispherical cakes of Cu-matte<sup>3</sup> upon cooling, if the Cu-content is much below 50 per cent., and horizontally if over 50 per cent., may be due in part to the separation of Cu (see also Ni-Cu matte).<sup>4</sup> The large needles of Cu found in some mattes, not to be confounded with moss-copper, are due to the reaction of  $\text{Cu}_2\text{S}$  upon CuO or  $\text{Cu}_2\text{O}$ .<sup>5</sup>

Matte is an excellent carrier of precious metals.<sup>6</sup> The leading reasons for this are that  $\text{Cu}_2\text{S}$  and  $\text{Ag}_2\text{S}$  form solid solutions,<sup>7</sup> the curve showing a maximum depression at  $677^\circ\text{C}$ .; that  $\text{Cu}_2\text{S}$  readily dissolves Au; that Cu easily alloys both with Ag (p. 22) and Au (p. 23); that Fe is a strong solvent for Au,<sup>8</sup> and that the same is the case<sup>9</sup> for  $\text{Au}_2\text{S}_3$  in the presence of  $\text{Ag}_2\text{S}$ . Little if any solvent action has been noticed with FeS for either  $\text{Ag}_2\text{S}$ <sup>10</sup> or  $\text{Au}_2\text{S}_3$ ,<sup>11</sup> and Fe has little affinity for Ag.<sup>12</sup> The equilibrium diagram for  $\text{Ag}_2\text{S}$ –FeS by Schoen<sup>13</sup> shows an eutectic with 11 per cent. FeS freezing at  $600^\circ\text{C}$ ., and a transformation at  $175^\circ\text{C}$ . characteristic for  $\text{Ag}_2\text{S}$ . The presence of PbS and ZnS in matte will not materially assist the collection of  $\text{Ag}_2\text{S}$ , provided  $\text{Cu}_2\text{S}$  is present, as both form eutectiferous alloys<sup>14</sup> in which the eutectic line extends to near the ordinates.

<sup>1</sup> Plattner, *Berg. Hüttenm. Z.*, 1855, XIV, 143.

Hampe, *op. cit.*, 1893, LII, 448.

Palmer, *Min. Sc. Press*, 1906, XCIII, 604.

Gibb-Philp, *Tr. A. I. M. E.*, 1906, XXXVI, 677.

Larison, *Min. World*, 1907, XXVII, 550.

<sup>2</sup> *Tr. A. I. M. E.*, 1908, XXXIX, 617.

<sup>3</sup> Bellinger, *Min. Ind.*, 1894, III, 229.

<sup>4</sup> Browne, *School Min. Quart.*, 1894–95, XVI, 297.

<sup>5</sup> Münster, *Berg. Hüttenm. Z.*, 1877, XXXVI, 220.

<sup>6</sup> Bolles, *Tr. A. I. M. E.*, 1905, XXXV, 666.

Fulton-Goodner, *op. cit.*, 1908, XXXIX, 584.

<sup>7</sup> Friedrich, *Metallurgie*, 1907, IV, 671.

<sup>8</sup> *Tr. A. I. M. E.*, 1886–87, XV, 767 (Spilsbury); 1889–90, XVIII, 454, 457 (Pearce); 1900 XXX, 769 (Carpenter); 1905, XXXV, 666 (Bolles); *Zt. angew. Chemie*, 1907, LIII, 291; *Rev. Mét.*, 1908, V, 188; *Metallurgie*, 1907, IV, 469 (Isaac-Tammann's solid solution curve).

<sup>9</sup> Muir, *Eng. Min. J.*, 1872, XIV, 56.

Pearce, *loc. cit.*

<sup>10</sup> C. J. B. Karsten, "System der Metallurgie," Reimer, Berlin, 1832, V, 525.

<sup>11</sup> Spilsbury, *loc. cit.*

<sup>12</sup> Spilsbury, Pierce, Bolles, *loc. cit.*

<sup>13</sup> *Metallurgie*, 1911, VIII, 737.

<sup>14</sup> Friedrich, *Metallurgie*, 1907, IV, 671, and 1908, V, 114.

In a copper matte  $\text{Cu}_2\text{S}$  is therefore the leading carrier of precious metals. The question is, how much Cu must be present to effect a complete collection. The consensus of metallurgists seems to be<sup>1</sup> that 0.5 per cent. Cu is sufficient, provided the degree of concentration is not too great. Carpenter<sup>2</sup> states that with little matte, this should contain 10 per cent. Cu, and that with much matte 2-3 per cent. Cu would be ample. Lang<sup>3</sup> calls attention to the formation temperature of the slag produced in smelting; if this be high, the matte will contain some metallic Fe, and this is a good collector for Au.

**120. Speise**—This is not often formed in the smelting of sulphide copper ores, as As and Sb are usually present in small amounts, and as most of the  $\text{As}_2\text{S}_3$  and  $\text{Sb}_2\text{S}_3$  is readily eliminated, either as oxide in the roasting which precedes a reducing fusion, or as sulphide in the pyritic smelting which treats raw ore. Sometimes speise is purposely produced in the treatment of ores containing Cu, Ni, As, and S in order to collect the Ni in the speise and the Cu in the matte; the speise, however, locks up considerable amounts of Cu. Some analyses of speise are given in Table 44.

TABLE 44.—ANALYSES OF COPPER SPEISE

Locality	Cu	Pb	Fe	Ni	Co	Zn	Sb	As	Ag	Au	S	Bi
Schmöellnitz <sup>4</sup> .....	12.99	0.09	12.63	1.40	0.09	...	60.00	7.42	0.36	0.06	2.04	1.26
Neusohl <sup>4</sup> .....	41.18	0.69	35.41	0.09	0.04	...	10.79	6.10	0.03	...	2.60	...
Brixlegg <sup>5</sup> .....	51.73	35.20	1.65	0.13	0.24	1.82	3.34	2.75	0.	175	1.38	1.63
Brixlegg <sup>5</sup> .....	25.85	16.68	22.17	1.60	1.11	3.31	13.50	11.04	0.	085	4.13	...
Pretoria <sup>6</sup> .....	52.50	0.25	3.60	...	...	...	38.00	2.00	1.59	...	2.06	...
England <sup>7</sup> .....	7.78	2.94	10.20	6.57	...	...	41.82	18.56	0.02	2.60	1.72	...

The treatment of speise consisted usually in a series of oxidizing roasts followed by reducing fusions, by means of which Ni with its great affinity for As is more and more concentrated, forming a nickel speise. More recently roast-smelting in the reverberatory furnace has become the favored method at Freiberg,<sup>8</sup> Oker,<sup>9</sup> and Brixlegg.<sup>10</sup> The latest proposition is that of Guillemain,<sup>11</sup>

<sup>1</sup> Rickard, "Pyrite Smelting," p. 134.

<sup>2</sup> *Op. cit.*, p. 34.

<sup>3</sup> *Op. cit.*, p. 37.

<sup>4</sup> Balling, C. A. M., "Metallhüttenkunde," Springer, Berlin, 1885, p. 192; *Min. Eng. World*, 1913, XXXVIII, 9.

<sup>5</sup> Kroupa, *Oest. Zt. Berg. Hüttenw.*, 1906, LIV, 73, 84.

<sup>6</sup> Bettel, *Eng. Min. J.*, 1891, LII, 74.

<sup>7</sup> McMurtry, *Tr. Inst. Min. Met.*, 1913, XXII, 50.

<sup>8</sup> Hübner, *Glück Auf.*, 1905, XLI, 6.

Hofman, *Min. Ind.*, 1905, XIV, 414.

<sup>9</sup> Huhn, *Glück Auf.*, 1905, XLI, 1145; *Min. Mag.*, 1906, XIII, 312; *Min. Ind.*, 1905, XIV, 414 (Hofman); 1906, XV, 286 (Austin).

<sup>10</sup> Kroupa, *Oest. Zt. Berg. Hüttenw.*, 1906, LIV, 73, 84.

Austin, *Min. Ind.*, 1906, XV, 286.

<sup>11</sup> *Metallurgie*, 1910, VII, 595; *Eng. Min. J.*, 1911, XCI, 50; *Min. Ind.*, 1910, XIX, 450.



to blast-roast speise in a Huntington-Heberlein pot. The experimental results have been most satisfactory. Converting speise with an addition of about 50 per cent. copper matte in a basic converter has been successful, while converting speise alone, has not. The electro-negative component of speise usually is As. In the analyses of Table 44, Sb prevails over As. There is an interesting record by Bettel<sup>1</sup> of the collection of Cu and Ag in an antimonial speise, by smelting in a reverberatory furnace; the analysis is given in Table 44; another record is that of McMurtry.<sup>2</sup>

**121. Slag.**—Compositions and Cu-contents of some blast-furnace slags are given in Table 28.

About twenty years ago, foul slag from a matte concentrating blast-furnace<sup>3</sup> of the Orford Copper Co., was partly freed from Cu by running it from the fore-hearth direct into one end of the ore-furnace a slight distance above the level of the tuyères. This worked satisfactorily, as long as the ore-furnace ran smoothly, without any obstructions forming to check the inflow of the slag. With ordinary care this could be avoided, but when accidents did occur, there was no end of trouble; hence, the method has been abandoned.

The Cu-losses<sup>4</sup> are caused by imperfect settling of matte (due to lack of time and temperature, insufficient difference in specific gravity, gas-flotation, mushiness of matte, viscosity of slag), by solution of metal, oxide or sulphide in slag, and by scorification of copper (silicate, perhaps ferrite). The second cause was once thought to be so insignificant that it could be neglected. The experiments of Wanjukow<sup>5</sup> prove that this factor has to be considered. The curves, Fig. 233, representing sesqui- and bi-silicates with 12 and 36 per cent. CaO, show how,

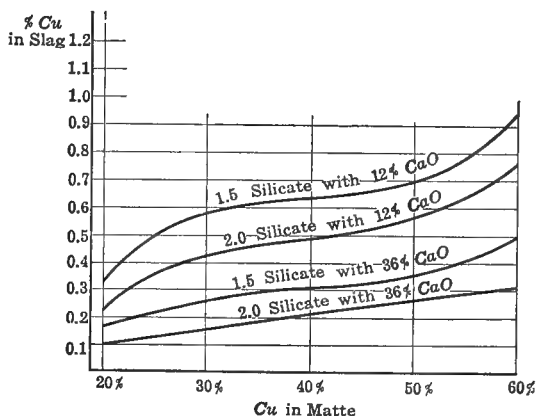


FIG. 233.—Relation of copper-content in slag to that in matte.

<sup>1</sup> *Eng. Min. J.*, 1891, LII, 74.

<sup>2</sup> *Tr. Inst. Min. Met.*, 1913, XXII, 50; *Min. Eng. World*, 1913, XXXVIII, 9.

<sup>3</sup> Eustis, W. E. C., Private Communication, April, 1894.

<sup>4</sup> Heywood, *Eng. Min. J.*, 1904, LXXVII, 395.

Wright, *Tr. A. I. M. E.*, 1909, XL, 492; 1910, XLI, 316.

Channing, *op. cit.*, 1910, XLI, 885; *Min. Sc. Press*, 1909, XCIX, 668.

Valley, *Eng. Min. J.*, 1905, LXXIX, 1223; *Ann. chim. analytique*, 1905, X, 193.

Heberlein, *Eng. Min. J.*, 1910, LXXXIX, 617.

Gabrill, *op. cit.*, 1910, LXXXIX, 776.

Schertel, L., Thesis, Freiberg, 1910.

<sup>5</sup> *Metallurgie*, 1912, IX, 148.

with as high a ratio of matte to slag as 2:5, the Cu-content of the slag increases with that of the matte. Wright finds that the Cu-content of slag increases with that of the matte produced, as shown in Fig. 234. Heywood, Fig. 235, states that

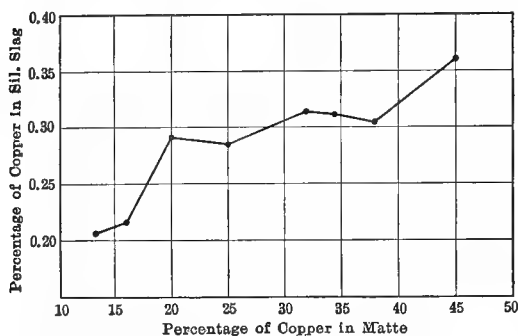


FIG. 234.—Relation of copper-content in slag and matte.

slags rich in iron and manganese carry more Cu than when rich in  $\text{SiO}_2$ . A relation between the percentage of  $\text{SiO}_2$  and the Cu-content has been noted in some cases; thus acid slags are to contain 0.5 per cent. and basic slags 1 per cent. of the Cu-content of the matte. The present knowledge of the different factors is still too incomplete to permit application of laws of physical chemistry for drawing general conclusions

which might assist in explaining satisfactorily individual cases. The Ag-content of slags appears to run parallel with that of Cu; that of Au shows no recognized regularity. Waste blast-furnace slag with 40- to 45-per cent. copper matte contains from 0.2-0.5 per cent. Cu.

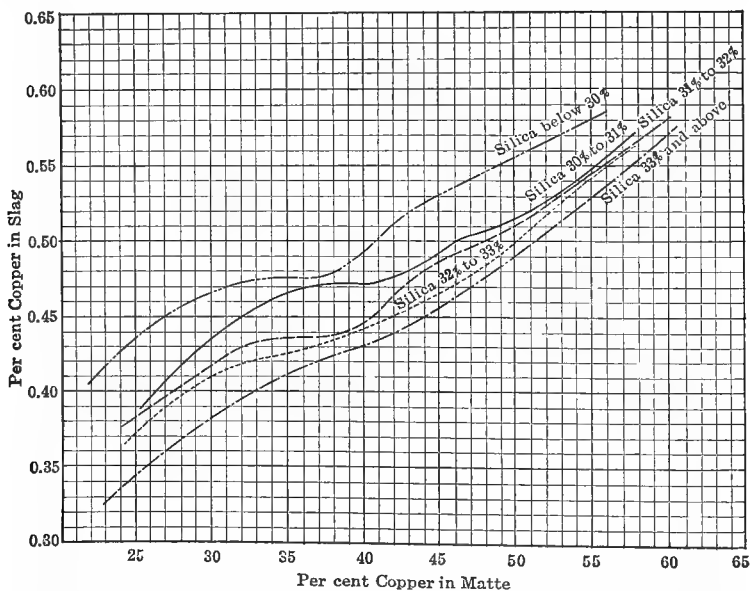


FIG. 235.—Relation of copper-content in slag to  $\text{SiO}_2$ - and  $\text{Fe(Mn)O}$ -content.

**122. Gases and Flue-dust.**—The average temperature of the waste gases at the open throat of a copper blast-furnace is low, in a reducing fusion ( $150^\circ\text{C}.$ ), in true pyritic smelting ( $250^\circ\text{C}.$ ). It is high in partial pyritic smelting (over  $300^\circ\text{C}.$ ).

Their velocity is also high on account of the small difference between tuyère- and throat-areas, an average figure being about 750 ft. per minute.<sup>1</sup> Though the temperature of the gases may drop to 100° C. when a new charge has been fed, it will rise in partial pyritic smelting to 600° C. by the time the next one is introduced, and at this temperature the velocity may rise to 1100 ft. per minute. In the downcomer, which carries away also the air that enters by the feed-doors, the velocity varies from 1000 to 1500 ft. per minute. The composition of the gases has been given on pp. 184, 194, 201, 225. The temperature will have to be reduced to 300° C. and the velocity to 200 ft. per minute in order that the fine dust may fall out.<sup>2</sup>

Studies carried on within the last six years upon the deposition of dust and fume in flues and chambers have been the cause of many advances made in the recovery of values otherwise lost. The installations of Cananea, Copper Queen, Anaconda, Great Falls, Mammoth, and Balaklala may serve as examples for the discussion of the subject.

At CANANEA<sup>3</sup> the blast-furnaces treat much fine material, 50 per cent. being smaller than  $\frac{1}{4}$ -in. The gas from a blast-furnace passes through a goose-neck into a balloon-flue common to eight blast-furnaces; from this the combined gases travel through two cross-over flues into a large dust chamber. Of the total dust collected, 55 per cent. was recovered in the balloon-flue, 2 per cent. in the cross-over flue, 28 per cent. in the first half of the chamber (the major portion lying beneath the cross-over flue), and the remaining 15 per cent. in the second half. A screen-analysis of the dust collected in the chamber showed that the bulk of the part which settled in the first half was of 60- and 80-mesh, and that the rest was 150- and 120-mesh and finer.

At the COPPER QUEEN works the experiments carried on by G. B. Lee<sup>4</sup> led to the conclusion that for that plant the flues and chambers need not exceed a length of 125 ft. as long as the velocity of the gases is not greater than 150 ft. per minute, even with dust of which 90 per cent. will pass a 200-mesh screen.<sup>5</sup>

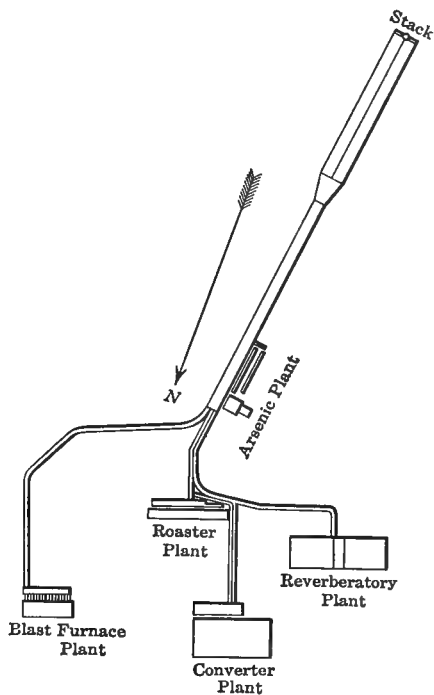


FIG. 236.—Plan of flues at Washoe smelter, Anaconda.

<sup>1</sup> Haas, *Eng. Min. J.*, 1910, XC, 814.

<sup>2</sup> Kiddie, *Tr. A. I. M. E.*, 1909, XL, 900.

<sup>3</sup> Shelby, *Eng. Min. J.*, 1908, LXXXV, 204.

<sup>4</sup> *Eng. Min. J.*, 1910, XC, 504.

<sup>5</sup> *Min. Sc. Press*, 1913, CVII, 929.

At ANACONDA<sup>1</sup> there is in operation for the collection of dust and fume a system of long flues through which the gases travel with diminishing temperatures and velocities.

The plant has three blast-furnaces 56 in. by 51 ft. and one 56 in. by 15 ft., 56 Evans-Klepetko MacDougall furnaces 16 ft. inner diameter, seven reverberatory furnaces 19 by 102-115 ft., and ten horizontal basic converters 8 ft. in diameter and 12 ft. 6 in. long.

The general plan of the condensation is shown in Fig. 236. The blast-furnace-, roaster- and converter-departments each have a dust chamber for collecting the coarse dust; in the reverberatory department the two Sterling boilers back of a furnace serve as catchers of coarse dust. Having been freed from coarse material, the dust and fume of the blast-furnaces travel through a flue of brick and steel construction (653 ft. long, 20 ft. wide, and 15 ft. high) to the main flue (1234 ft. long, 60 ft. wide, and 20 ft. high) of I-beam and brick-arch construction, and enter the twin flue (995 ft. long, 120 ft. wide, and 20 ft. high),

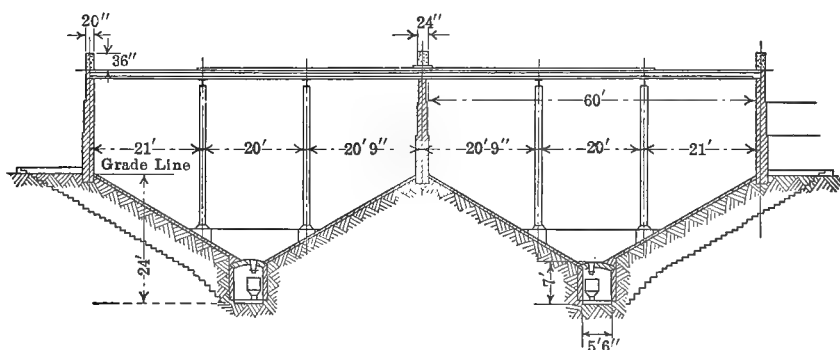


FIG. 237.—Twin condensation-flue at Washoe smelter, Anaconda.

shown in cross-section in Fig. 237, leading to the stack (300 ft. high and 30 ft. inner diameter). The gases thus travel 4182 ft. The roaster-gases travel 3017 ft.; the converter-flue is 7 by 7 ft., and the gases travel 3662 ft.; the reverberatory gases travel 3782 ft. Near the foot of the 60-ft. main flue is the arsenic plant,<sup>2</sup> which treats the dust recovered in the 120-ft. flue. The velocity of the gases in one of the double flues is 12 ft., and in the stack 16-17 ft. per second. There are recovered in the flue of the double main 0.114 lb. dust per 1000 cu. ft. gas, and 1,450,000,000 cu. ft. gas pass through it per day. The dust that passes off into the open is finer than 200-mesh; an analysis gave:  $\text{SiO}_2$  4.19,  $\text{Al}_2\text{O}_3$  3.14,  $\text{Fe}_2\text{O}_3$  2.78,  $\text{CaO}$  0.50,  $\text{MgO}$  0.69, total S 10.05, total  $\text{SO}_3$  23.25, free  $\text{SO}_3$  3.60, Cu 0.84, Zn 9.50,  $\text{As}_2\text{O}_3$  34.34, Pb 10.80,  $\text{Sb}_2\text{O}_3$  1.17,  $\text{Bi}_2\text{O}_3$  1.15,  $\text{Na}_2\text{O}$  0.49,  $\text{K}_2\text{O}$  0.42, C 0.8, Se 0.28, Te 0 per cent., and Au 0.005 and

<sup>1</sup> McDougal, *Canad. Min. Rev.*, 1905, XXIV, 26.

Austin, *Tr. A. I. M. E.*, 1906, XXXVII, 478.

Dunn, *op. cit.*, 1913, XLVI.

<sup>2</sup> Elton, *Tr. A. I. M. E.*, 1913, XLVI.

Ag 4.9 oz. per ton. An average sample of the dust collected in the 120-ft. main flue gave Cu 0.986 and  $\text{As}_2\text{O}_3$  34.2 per cent., and Au 0.0058 and Ag 4.44 oz. per ton.

At GREAT FALLS<sup>1</sup> the Roesting wire system<sup>2</sup> for retarding the gas current by increasing the resistance through suspended wires is in successful operation. The general arrangement of plant and new system of condensation is shown in Fig. 238, a cross-section of the dust chamber in Fig. 239, and partial longitudinal section in Fig. 240. The plant has 24 Evans-Klepetko-MacDougall furnaces (16 ft. inner diameter), three gas-fired reverberatory smelting furnaces (42 ft. 6 in. by 15 ft. 9 in.) with regenerative chambers, five blast-furnaces (54 by 160 in.), seven upright converters<sup>3</sup> (7 ft. diameter and 14 ft. 7 in. high). Elaborate working experiments were carried on with various dust-arresting devices before the present system of condensation was introduced. The results of these tests are represented graphically in Fig. 241. Curves 32 and 34, representing gases passing through an open or ordinary flue, show that under the conditions of the tests only 30-40 per cent. of the dust was collected. With narrow plates suspended in such a way that the gas-current strikes the edge (Freudenberg plates)<sup>4</sup> matters are improved, curve 33, as the collection of dust is over 40 per cent. By suspending in the flue long narrow plates in such a way that the gas-current strikes the faces, a great deal more dust is precipitated as seen in curve 36 ( $3\frac{1}{8}$ -in. baffle-plates), and in the entrance- and exit-parts of curve 35 ( $6\frac{1}{4}$ -in. baffle-plates). The wider plates reducing the cross-sectional area 50 per cent. were more effective as dust catchers than the narrower which reduce it 25 per cent., but both strongly interfere with the draft. The difference between open- and open- and baffled-flue is shown strikingly in curve 35. The action of suspended wires is seen in curve 39 ("wire baffles"). The wire-baffles do not obstruct the draft as do plate-baffles and at first do not collect as much dust, but make up for this later on, causing 84 per cent. of the dust to separate, which is more than the other arresting devices. Curve 38 brings out the difference in settling power of an open flue and one provided with wires. In curve 37 is represented the effect sudden reductions and enlargements of area of flue at certain distances have upon the settling of dust. In the tests, the flue, 304 ft. long and 4 ft. by 4 ft. 6 in. = 16 sq. ft. area, was partly closed, 100 and 104 ft. from the ends, by two partitions each having in the center an opening 1 ft.  $6\frac{1}{2}$  in. in diameter = 1.8 sq. ft. area. This arresting device is effective as a collector of dust and is cheap to build. With a reduction of area of from 18 to 1.8 sq. ft. the interference with the draft was too great to work satisfactorily, but the data show that the method is promising.

In the new flue-system, Fig. 238, there have to be considered the dust-

<sup>1</sup> Herrick, *Mines and Minerals*, 1909, xxx, 257.

Goodale, *Tr. A. I. M. E.*, 1909, xl, 891.

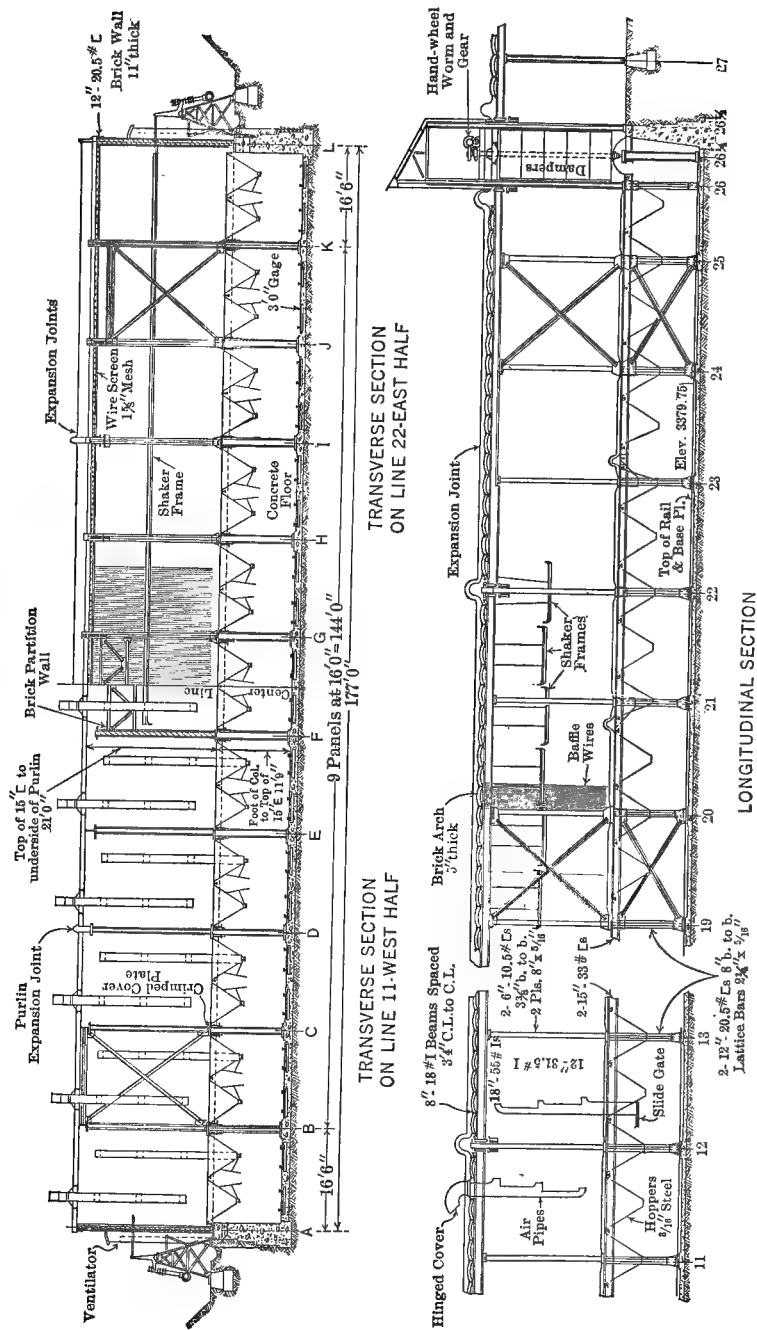
Goodale-Kleping, *op. cit.*, 1913, xlvi.

<sup>2</sup> Hofman, "General Metallurgy," 1913, p. 846.

<sup>3</sup> Since the basic converter has replaced the acid, the sizes of vessels have been increased and the number decreased; see § 176.

<sup>4</sup> Hofman, "General Metallurgy," 1913, p. 845.





FIGS. 239-240.—Transverse and longitudinal sections through dust-chamber of Great Falls.

chamber, the connecting flue leading to the stack, the flues leading to the dust-chamber, and the results obtained.<sup>1</sup>

The brick dust-chamber, 357 ft.  $11\frac{1}{8}$  in. long by 176 ft. wide by 27 ft. high, is supported, Figs. 239 and 240, by columns, 11 ft. 9 in. high, so as to leave room for the bottom-discharge of dust through sheet-steel hoppers (over 1000 in number, arranged in 22 lines) into cars running on tracks of 3-ft. gauge. The chamber is divided longitudinally by a partition wall so that by means of dampers the gas-current can be made to travel through either half. At the inlet of the cham-

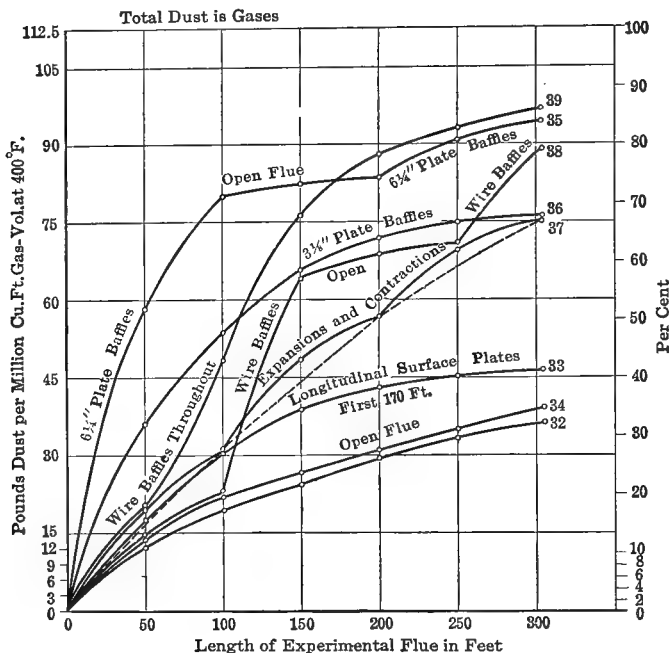


FIG. 241.—Relative efficiency of dust-arresting devices, Great Falls.

ber a space is left clear to afford an unobstructed passage for the gases that they may distribute themselves over the full width of the chamber. In order to cool the gases, 22 air-admission pipes, Fig. 240, enter from top and bottom. The wires are suspended in two divisions. From the entrance of the chamber to a distance of 150 ft., and back from the exit also for 150 ft., the space is fully occupied by wires; the intervening space of 47 ft. is left free from wires. The purpose of this arrangement was to collect dust in the entrance- and fume in the exit-division. The wired part of the chamber holds about 1,200,000 steel wires spaced 2.3 in. center to center; for a distance of 51 ft. from the inlet the wires are No. 8 W. & M. gauge and 16 ft. long; the rest of the wired chamber has No. 10 wires 20 ft. long. For the support of the wires, steel-wire netting, Figs.

<sup>1</sup> Some minor changes not shown in the drawings have been made since the new flue-system went into operation June 12, 1909, but these are passed over.



242 and 243, of  $1\frac{3}{8}$ -in. mesh is bolted to the I-beams of the roof; the baffle-wires are bent at one end to the form of a shepherd's hook and suspended from alternate intersecting points; they are thus staggered, which aids in arresting dust.

For the shaking of the wires to dislodge adhering dust, angle-iron frames, Fig. 240, 10 ft. wide extending from the side-walls to near the partition wall, are suspended by hangers about 10 ft. long. A frame has a wire netting with openings 4 by 7 in., is shaken for 30 min. at intervals 60–90 days by a connecting-rod extending through the flue-wall and attached to a bell-crank lever actuated by an eccentric with a stroke of 9.5 in. and 60 strokes per minute; the eccentrics on each side of the chamber are carried by a line-shaft operated by an electric motor.

The flue connecting the dust-chamber with the stack, Fig. 238, is (section *EE*) 48 ft. wide by 21 ft. high. At its terminus it is divided into two branches (section *FF*). The stack is 506 ft. high and 50 ft. in diameter at the top; it is circular inside, octagonal outside for 46 ft. from base, and circular for the remainder of the height (drawings in reference).

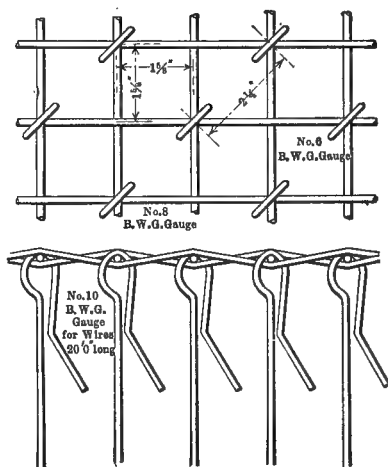
The gases from the converters, Fig. 238, pass through the converter-flue which joins the flue from the MacDougall roasters (section *CC*) as this enters the cross-take flue (section *DD*). The gases from the reverberatory furnaces pass into a collecting flue before they either enter the dust-chamber, or are by-passed around the dust-chamber to the flue leading to the stack. The gases from the blast-furnaces (section *BB*) travel through their main to the cross-take flue.

The temperature of the gases (excluding reverberatory-furnace gases) at the entrance of the dust-chamber is  $163^{\circ}\text{C}$ . and at the exit  $135^{\circ}\text{C}$ .; near the chimney at the branching of the connecting flue (including the reverberatory-furnace gases), the temperature is  $163^{\circ}\text{C}$ .

Table 45 gives temperature- and draft-readings in the leading divisions of the flue-system; Table 46 the velocities, volumes, average temperatures, and weights of gases; and Table 47 the amounts of gas produced per furnace and per ton of charge.

Practically all the dust and most of the metallic fume are recovered. The escaping gases contain free  $\text{H}_2\text{SO}_4$  22.23,  $\text{SiO}_2$  2.30,  $\text{Cu}$  0.70,  $(\text{FeAl})_2\text{O}_3$  7.08,  $\text{S}$  6.67,  $\text{Sb}_2\text{O}_3$  1.47,  $\text{Bi}_2\text{O}_3$  0.81,  $\text{PbO}$  0.49,  $\text{CaO}$  0.18,  $\text{ZnO}$  3.31,  $\text{O}$  (calculated for  $\text{S}$ ) 10.23 per cent.

In Fig. 244 is shown the relative deposition of dust through the chamber; the superimposed fine full-drawn lines represent the outline of the dust-chamber,



FIGS. 242–243.—Method of hanging wires in dust-chamber at Great Falls.

TABLE 45.—TEMPERATURE- AND DRAFT-READINGS

Locations of readings in Fig. 238	Elevation	Temperature in flue, F.°	Temperature of atmos- phere, F.°	Draft-readings, in. water	
				Impact tube	Static tube
(A) Blast-furnace.....	3,338	391	80	1.12	1.16
(B) MacDougall.....	3,361	419	80	0.94	0.98
(D) Cross-take.....	3,413	358	80	0.88	0.97
(D) Cross-take.....	3,413	346	70	0.94	1.01
(L) Connecting flue.....	3,413	312	70	2.20	2.26
(U) Near chimney.....	3,570	310	70	1.80	1.84

TABLE 46.—VELOCITIES, VOLUMES, AVERAGE TEMPERATURES, AND WEIGHTS OF GASES

Loca- tions in Fig.238	Date, 1911	No. and kind of furnaces	Average temper- ature, F.°	Clear area of flue, sq. ft.	Vel. in ft. per sec.	Vol. at observed temperature, cu. ft. per min.	Pounds gas per min.	Pounds gas per furnace per min.
A.....	Apr. 6-8.....	4 B. F....	345	401.6	17.26	415,960	18,510	4.063
B.....	Apr. 6-8.....	10 MacD...	352	169.0	17.50	253,500	10,980	1.100
C.....	Apr. 6-8.....	5 Conv....	303	78.5	50.37	213,630	9,840	1,970
G.....	Mch. 21-24....	2 Rev.....	496	152.5	43.34	396,700	14,530	7,270
D1.....	Apr. 6-8.....	4 B. F....	331	636	21.80	859,300	38,190	.....
		5 Conv....						
E1.....	Mch. 21-24..	4 B. F....	286	977	15.51	901,400	42,280	.....
		6 MacD...						
F.....	Mch. 21-24..	5 Conv....	311	977	21.03	1,234,900	56,110	.....
		6 MacD...						
E2.....	Apr. 10.....	2 Rev.....	290	977	15.54	910,950	42,270	.....
		4 B. F....						
D1.....	Apr. 10.....	10 MacD...	290	977	15.54	910,950	42,270	.....
D1.....	Apr. 10.....	5 Conv....	322	636	22.74	867,760	38,700	.....

TABLE 47.—AMOUNT OF GAS PER FURNACE AND PER TON OF CHARGE

Kind of furnace	Observed temperature correspond- ing to given volume, F.°	Rate per min.		Rate per 24 hr.		Aver- age tons charged	Per ton of charge	
		Cu. ft.	Lb.	Cu. ft.	Lb.		Cu. ft.	Lb.
Blast.....	345	103,990	4,630	149,745,600	6,667,200	391.61	384,900	17,000
MacDougall....	352	25,350	1,100	36,504,000	1,584,000	70.7	516,300	22,400
Converter.....	303	42,730	1,970	61,531,200	2,836,800	32.03	1,922,900	88,600
Reverberatory..	496	198,350	7,270	285,624,000	10,468,800	188.5	1,515,200	55,500

<sup>1</sup> Includes flux but does not include fuel.

<sup>2</sup> Tons copper produced per converter day.

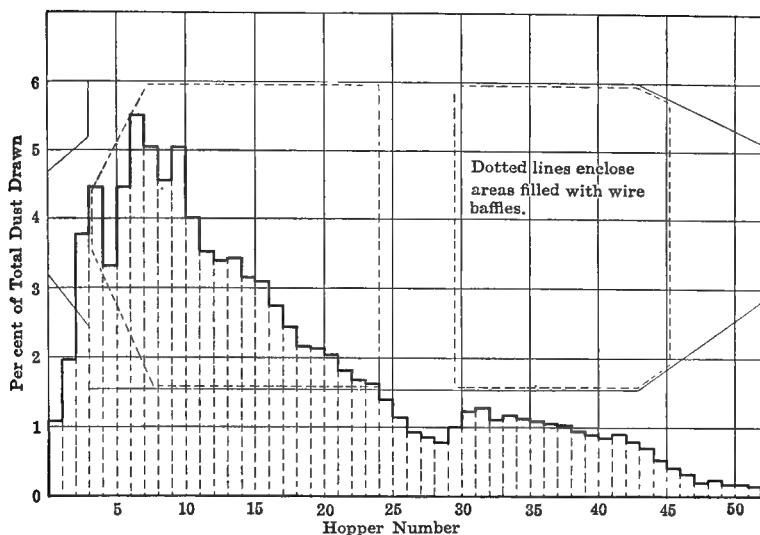


FIG. 241.—Relative deposition of dust through dust-chamber, Great Falls.

TABLE 48.—QUANTITY AND ANALYSES OF FLUE-DUST

Name of flue	Tons dust		Cu per cent.	Ag oz. per ton	Au oz. per ton	Insol.	SiO <sub>2</sub>	FeO	Al <sub>2</sub> O <sub>3</sub>	CaO	S
	Total for 41 months	Average per month									
Blast-furnace.....	87,020	2,122	8.08	2.7	0.019	34.7	26.8	33.0	7.1	1.7	16.1
MacDougall furnace.	18,741	457	10.22	3.6	0.023	37.6	29.0	27.1	7.5	0.3	21.3
Up-take and cross-take	17,360	423	12.59	4.1	0.026	34.8	26.0	27.2	7.2	0.7	19.5
Main dust-chamber..	64,048	1,562	8.61	3.3	0.020	33.3	23.6	14.5	8.0	0.7	11.8
Connecting flue <sup>1</sup> .....	4,000	98	3.09	3.1	0.012	12.6	8.5	5.4	4.0	0.1	10.6
Total.....	191,169	4,662	.....	.....	.....	.....	.....	.....	.....	.....	.....

<sup>1</sup> Weight estimated. Average analysis is from sample taken in June, 1912, at different points from dust-chamber to chimney.

the dotted lines the areas filled with wires. The quantities and analyses of dust collected in a period of 41 months are shown in Table 48. The distribution of the material is shown in Table 49.

TABLE 49.—PERCENTAGE DISTRIBUTION OF MATERIAL IN FLUE SYSTEM

	Weight	Copper	SiO <sub>2</sub>
Blast-furnace flue.....	39.3	41.4	47.3
MacDougall-furnace flue.....	8.5	11.3	11.0
Cross-take flue.....	7.8	12.9	8.8
Main dust-chamber.....	28.9	32.5	30.7
Connecting flue.....	1.8	0.7	0.7
Stack discharge.....	13.7	1.2	1.5
Totals.....	100.0	100.0	100.0

THE MAMMOTH SMELTERY, KENNETT, CAL.<sup>1</sup>—The method for the recovery of flue-dust is by filtration. The plant has five blast-furnaces, 50 by 180 in., in which partial pyritic smelting is practised. During the summer and autumn two furnaces are in blast, during the winter four. The cooling system is not large enough to handle in the warm season more than the 250,000 cu. ft. gas per minute at 0° C. that come from two blast-furnaces and the converters at a temperature of 275° C. The matte with Cu 20–30 per cent. is converted in two stands with acid-lined vessels 96×150 in.<sup>2</sup>

The general arrangement of the condensation plant is given in Fig. 245. The gases from the blast-furnaces and converters travel through two long brick flues, in which most of the dust is settled, to the base of an old stack (marked 18×200

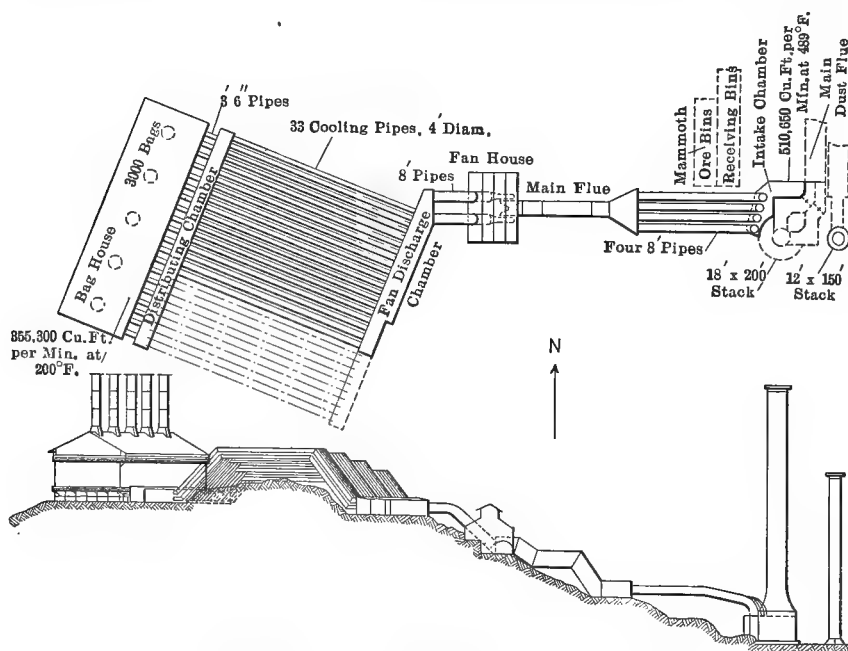


FIG. 245.—Condensation plant of Mammoth smelter, Kennett, Cal.

ft. in Fig. 245) and thence through four steel pipes, 8 ft. in diameter, to a steel collecting chamber, 42 ft. wide by 15 ft. high, which contracts toward the exit and ends in a steel flue, 15 by 15 ft., terminating in the fan house. Small amounts of ZnO and ZnSO<sub>4</sub> are collected in the flues and chamber. In order to cool the gas to 100° C. and less, air is admitted to the fan discharge chamber (later it will be blown into the distributing chamber in front of the baghouse). In the fan-

<sup>1</sup> Campbell, *Min. Sc. Press*, 1908, xcvi, 30.

Martin, *Min. Eng. World*, 1908, xxix, 309.

Rice, *Eng. Min. J.*, 1911, xci, 614.

Nevins, *Min. Sc. Press*, 1913, cvi, 374.

Martin, *Mines and Minerals*, 1913, xxxiii, 323.

<sup>2</sup> Kervin, *Eng. Min. J.*, 1914, xcvi, 713.

house are two Sirocco fans 11 ft. in diameter making 219 r.p.m., each driven by a 400-h.p. General Electric induction motor. Below the fans there is a vacuum of 1.7; above, a pressure of 3 in. water. At the entrance of the two 8-ft. delivery pipes into the fan-discharge chamber, 20 by 15 ft. and 160 ft. long, is a machine for feeding zinc oxide<sup>1</sup> to neutralize  $\text{SO}_3$  that has remained uncombined. Most of the  $\text{SO}_3$  in the blast-furnace gas has formed  $\text{Zn}_2\text{SO}_4$  with the  $\text{ZnO}$  formed in smelting the charge containing about 4 per cent. Zn. The gases from the converters are similarly treated with  $\text{ZnO}$  and powdery  $\text{Ca}(\text{OH})_2$  before they join the blast-furnace gases. From the chamber the gases travel through 39 steel cooling-pipes, 4 ft. in diameter and 200 ft. long, supported by iron rings held in wooden stands. The pipes discharge into the baghouse distributing chamber; each is provided with a butterfly valve so that when several are closed the small amount of dust collected in the others may be swept out by the stronger gas-current passing through them. From the chamber, 13 ft. 6 in. by 14 ft. and 210 ft. long, 20 short pipes, 3 ft. 6 in. in diameter, provided with flap-valves, deliver the gas into the baghouse which is 210 by 63 ft., has 3000 bags, equivalent to 25,000 sq. ft. filtering surface per ton of fume per day.<sup>2</sup> The baghouse has the usual thimble-floor; beneath it are 20 transverse hoppers for collecting the fume to be discharged through circular gates into cars (a continuous discharge is to be installed), dampened, and briquetted. The filter chamber, 40 ft. high, is divided into five bays, each with 600 bags 34 ft. long and 18 in. in diameter, some of wool, others of cotton. The bags, 3-10 in. apart, are placed in rows 21-28 in. center to center. Each bay has a monitor tower, 20 ft. square and 125 ft. high, which draws in enough air to dilute the  $\text{SO}_2$ -content of the filtered gas to 0.75 per cent. vol. The dust adhering to the bags is loosened by means of Benedickt shakers.<sup>3</sup> The gas-pressure in the baghouse is 1.7 in. water. Men entering the filter chamber carry Draeger fire-fighting helmets.

The crew of the plant for 24 hr. is made up of 1 foreman and 12 men, 4 on an 8-hr. shift. The cost of installation is \$800 for 1000 cu. ft. of gas per minute. With two blast-furnaces there are filtered per minute 250,000 cu. ft. gas; these furnish in 24 hr. 10 tons of fume, which consists largely of  $\text{ZnO}$  and  $\text{ZnSO}_4$ , runs high in Ag, carries some Au and Pb, and Cu 0.5 per cent. An analysis quoted by Nevius<sup>4</sup> shows: Cu 1.04, Insol. 7.8, Fe 6.2,  $\text{CaO}$  1.8, Pb 7.0, As 4.3,  $\text{ZnO}$  4.8,  $\text{ZnSO}_4$  47.2 per cent., Au 0.03 and Ag 4.08 oz. per ton.

BALAKLALA SMELTERY, CORAM, CAL.—Here the Cottrell system of electric condensation<sup>5</sup> was in operation before the plant was shut down. In this process a high-potential direct current jumping through an air-space from needle-points of one pole to the plate of the other causes particles of suspended dust and vapor to travel toward the plate at a speed which is proportional to the charges and to the potential gradient between point and plate.

<sup>1</sup> Sprague process: Hofman, "General Metallurgy," 1913, p. 849. Sprague, *Eng. Min. J.*, 1910, LXXXIX, 520.

<sup>2</sup> Sprague, *loc. cit.*

<sup>3</sup> Hofman, "General Metallurgy," 1913, p. 855.

<sup>4</sup> *Loc. cit.*

<sup>5</sup> Hofman, *op. cit.*, 1913, p. 859; Cottrell, *J. Ind. Eng. Chem.*, 1911, III, 542.

The smeltery treated 700–1000 tons sulphide ore with Cu 2.5–3.0 per cent., S 30 per cent., and more or less Zn; 90 per cent. was smelted in blast-furnaces; 10 per cent. was roasted in MacDougall furnaces and smelted in oil-fired reverberatory furnaces; the matte was converted in two stands. The gas from these departments entered a common flue, 18 by 20 ft.; it varied with operating conditions from 250,000 to 500,000 cu. ft. per minute; the linear velocity in the flue varied correspondingly from 10 to 20 ft. per second; the temperature at the inlet-flue ranged from 100–150° C.

A plan and section of the condensation plant, costing \$100,000, are shown in Figs. 246 and 247. The gases from the smelting and roasting furnaces are collected in the inlet-flue, Fig. 246, pass through nine precipitation chambers connected in parallel, are assembled in the outlet-flue, and delivered by two fans into

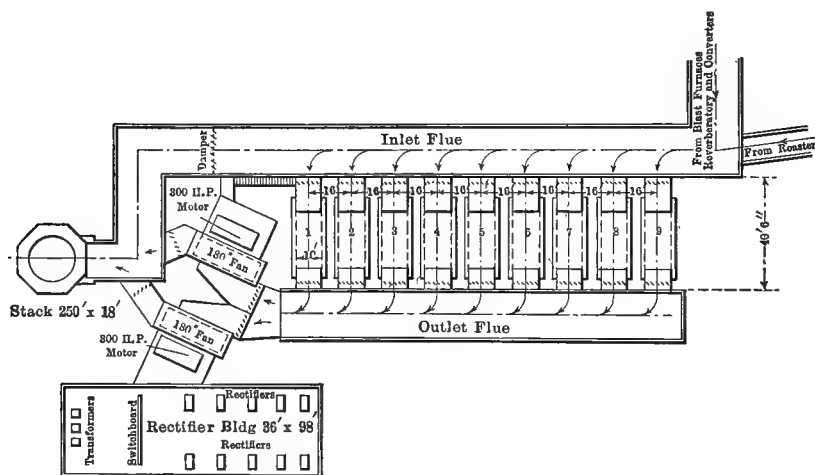


FIG. 246.—Cottrell electric condensation plant at Balaklala smeltery, Coram, Cal.

the chimney; the fans suck in enough air to reduce the  $\text{SO}_2$ -content of the cleaned gas to 0.75 per cent. or less.<sup>1</sup> In the rectifier an alternating current of 2300 volts is transformed up to 25,000–30,000 volts, rectified into an intermittent direct current, and distributed to the precipitating chambers. In the cross-section of a precipitating chamber, Fig. 247, the twenty-four vertical double lines represent the collecting electrodes (6 in. wide, 10 ft. high, of No. 10 sheet iron) carried by bars direct connected with the frame of the chamber and thus grounded. The vertical dotted lines represent the discharge electrodes consisting of two iron-wire strands between which is twisted the discharge material—asbestos and mixed preparations; they are spanned by springs between busbars carried by insulators placed outside and enclosed in auxiliary chambers through which passes an air-current to prevent conductive dust or fume from settling.<sup>2</sup> The cam, shown on the left side, and

<sup>1</sup> Later, chambers 1 to 9 were connected up in three series receiving current with increasing potential.

<sup>2</sup> The wires were replaced by split iron rods holding "micanite" formed to have saw-teeth, as the wires became clogged with zinc oxide.

the shaker-rod, extending across the chamber, intended to remove precipitate, were found to be unnecessary, as the electrodes could be easily shaken by hand from the top; this had to be done every 6 or 8 hr. The dust collected in the fume-hopper and was removed by a conveyor.

The average power-consumption was 120 kw.; the plant required one foreman, one man in the rectifier house, and two in the precipitation house. With all parts under good control the saving of suspended matter was over 90 per cent., the average was nearer 75 per cent. The plant was closed before all the details had been perfected.

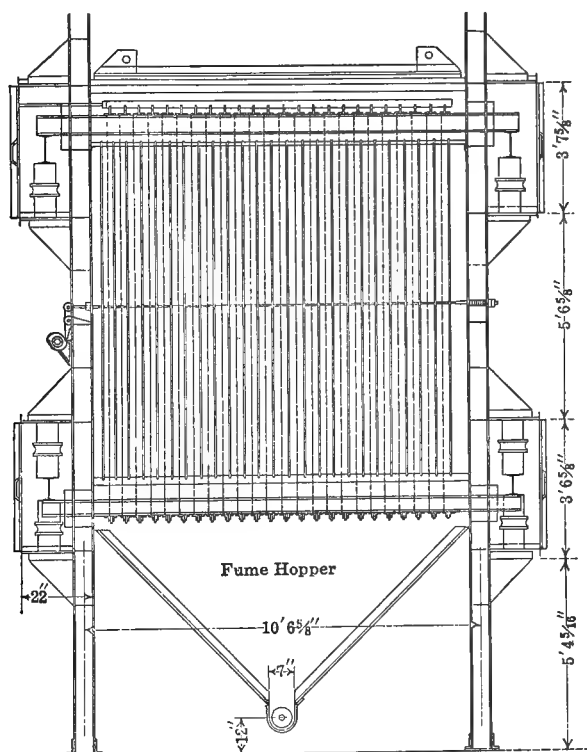


FIG. 247.—Cottrell electric condensation plant at Balaklala Smelter, Coram, Cal.

GARFIELD SMELTERY, GARFIELD, UTAH.<sup>1</sup>—At these works a plant of one hundred and fifty 5-in. pipe-electrodes, similar to those discussed in § 173, each 10 ft. long, operated under 20,000 volts, was installed for experimental purposes near the chimney, which took gases from blast-furnaces and MacDougall calciners.

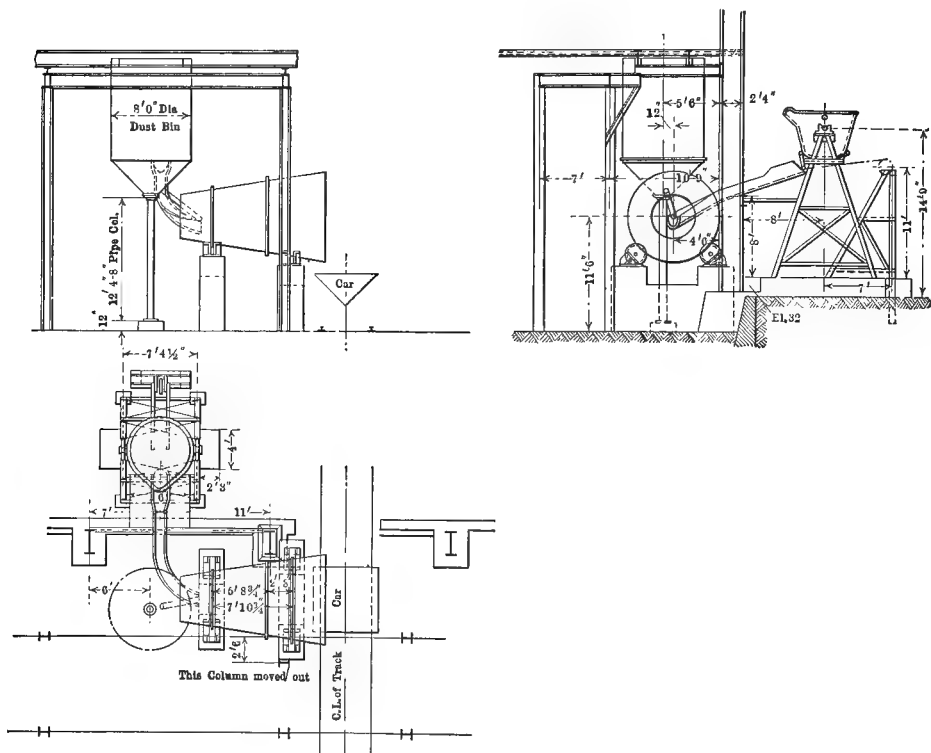
The apparatus treated from 4000 to 9000 cu. ft., blast-furnace gas per min.; 8 hours were given to a test; the treated gas was sampled continuously in order to determine the amount of clearance. Tests lasting several weeks gave the following average results: With velocities of from 5

<sup>1</sup>Private communication, W. H. Howard, December, 1913.

to 7.5 ft. per sec. in the electrodes and a temperature of  $90^{\circ}\text{C}$ ., 95 per cent. clearance was obtained, all the dust being collected; the remaining 5 per cent. consisted mainly of moisture and a small amount of acid. With velocities of from 3 to 3.5 ft. per sec. and a temperature of  $85^{\circ}\text{C}$ ., perfect clearance was obtained.

With roaster gas having a velocity in the electrodes reaching 7.5 ft. per sec. and a temperature of  $85^{\circ}\text{C}$ ., practically complete clearance was obtained.

Observations on the poisonous effects of copper when melting in an electric furnace have been published by Hansen.<sup>1</sup>



FIGS. 248-250.—Mixer for flue-dust and converter slag, Copper Queen smelter, Douglas, Ariz.

**123. Treatment of Flue-dust.**—The treatment of flue-dust varies with the character of the plant.

If reverberatory-smelting is carried on, the flue-dust is usually added to the reverberatory-charge. At Morenci, Ariz.,<sup>2</sup> it is charged into an oil-fired 50-ft. reverberatory furnace which serves as a settler for blast-furnace slag.

Incorporating the dust in converter-slag was in successful operation at the Copper Queen smelter, Douglas, Ariz., up to the time of the erection of the

<sup>1</sup> *Met. Chem. Eng.*, 1911, IX, 67.

<sup>2</sup> Douglas, *Eng. Min. J.*, 1907, LXXXIII, 198.



reverberatory division for smelting roasted concentrate.<sup>1</sup> Figs. 248-250 show side- and end-elevations and plan of the apparatus. The leading parts are a dust-bin with bottom-discharge, a tilting converter-ladle emptying into an inclined trough, and an inclined conical drum built of ribbed cast-iron sections, 1.5 in. thick, running on friction rollers. The discharges of dust-bin and converter-ladle meet at the upper end of the drum; the slag readily takes up the dust in its passage through the drum forming balls varying in size from 0.5 to 6 in. in diameter.

At Cananea<sup>2</sup> the dust is incorporated in converter slag by feeding the dust from a hopper with spout into the bowl of a slag-car while converter slag is being poured from the same level through a trough. The dust is drawn down into the slag and becomes well mixed. When the bowl is filled, the slag is poured down an incline over which it rolls as a viscous mass and balls up, forming balls 0.5-12 in. in diameter which are sprayed with water to be cooled and rendered porous.

A third method of compacting is that of agglomeration.

Heberlein<sup>3</sup> patented a process for agglomerating iron or manganese ore, blue billy, flue-dust, etc., which consists in adding carbonaceous fuel to the charge and blowing it in an Huntington-Heberlein pot as in the ordinary operation of blast-roasting. This process is in operation<sup>4</sup> at the works of the Zenith Furnace Co., Duluth, Minn.

Two 100-ton Dwight-Lloyd straight-line sintering machines treat the flue-dust of the smelter of the Mason Valley Mines Co., Thompson, Nev.<sup>5</sup> A screen-analysis of an average sample of dust gave: On 20-mesh, 1 per cent.; 20- to 40-mesh, 12.3; 40- to 80-mesh, 29.1; 80- to 100-mesh, 22.7; 100- to 150-mesh, 13.5; 150- to 200-mesh, 10.8; through 200-mesh, 16 per cent. The finest dust gave upon sifting: On 20-mesh, nil; 20- to 40-mesh, nil; 40- to 80-mesh, 0.1; 80- to 100-mesh, 2.9; 100- to 150-mesh, 0.5; 150- to 200-mesh, 3.5; through 200-mesh, 93.0 per cent. This is mixed with the coarser dust. A chemical analysis of average dust showed: Cu 3.5, Fe 18.5, SiO<sub>2</sub> 36.5, CaO 12.0, S 4 per cent. As the fuel value of the material is too low to permit treating the dust alone, there is mixed in 25 per cent. of fine sulphide material, with Cu 4.0, Fe 18, SiO<sub>2</sub> 37, CaO 12, Al<sub>2</sub>O<sub>3</sub> 10, and S 12 per cent., and about 3 per cent. coke. The coke is omitted when the S-content of the mixture is 7-8 per cent.; considerable attention has to be given to regulating the amount of water that is added to the charge. The grates of the machine are of malleable iron.

The charge is made up as follows: The dust runs from a hopper-bottom flue into a drag-conveyor which delivers to the boot of an elevator emptying into a bin having a feed-belt beneath the discharge. Fine ore and coke are trammed to bins alongside which are similarly equipped. From the three bins forming a

<sup>1</sup> Editor, *Eng. Min. J.*, 1913, xcvi, 627.

<sup>2</sup> De Kalb, *Min. Sc. Press*, 1910, ci, 9.

<sup>3</sup> *Oest. Zt. Berg. Hüttenw.*, 1908, xlvi, 555; *Min. Ind.*, 1908, xvii, 605.

<sup>4</sup> *Eng. Min. J.*, 1913, xcvi, 394.

<sup>5</sup> Private Communication of J. Labarthe and A. J. McNab, August, 1913.

group any desired amount can be delivered to a common conveyor-belt by adjusting the speeds of the three belts, or the sizes of the openings, or both. The common conveyor drops the mixture into the boot of an elevator which discharges on to the conveyor-belt in the sintering plant which feeds the two machines. These treat in 24 hr. 100 tons of mixture each and require 40 gal. of naphtha. The labor for each machine is one furnaceman, one helper, and one man moving cars. With two machines, one man with motor moves cars and takes away sinter.

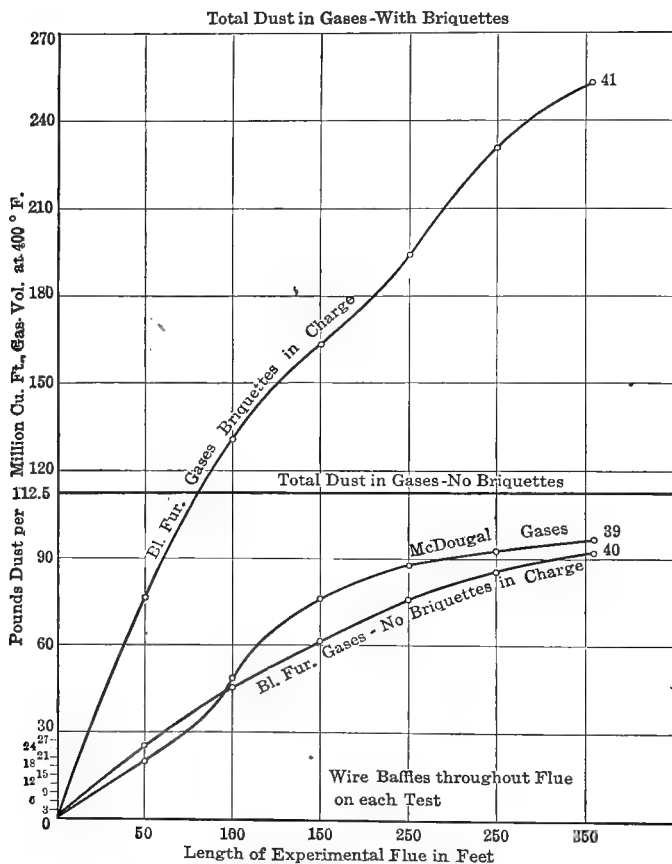


FIG. 251.—Cumulative dust-curves of blast-furnace-charges with and without briquettes, and of MacDougall calciners.

BRIQUETTING FLUE-DUST is a method of compacting flue-dust which was in more general use a few years ago than at present.

At Anaconda<sup>1</sup> the Chambers Bros. (Philadelphia, Pa.) No. 7 auger end-cut soft-mud brick machines<sup>2</sup> are in operation. One machine makes in 24 hr. 840

<sup>1</sup> Austin, *Tr. A. I. M. E.*, 1906, XXXVII, 460.

<sup>2</sup> Hofman, "General Metallurgy," 1913, p. 643.

tons of briquettes, weighing 5-10 lb., with 9 men on a shift. The mixture is made up of  $\frac{1}{3}$  screenings from first-class ore,  $\frac{1}{3}$  table concentrate, and  $\frac{1}{3}$  concentrator slime; to this is added 5 per cent. washed coke from the ash-pit droppings of the reverberatory smelting furnaces. The handling of material is mechanical throughout; the briquettes are stored in bins, from which they are drawn, imperfectly dried, into the charging cars of the blast-furnaces.

The investigations of Goodale and Klepinger<sup>1</sup> into the condensation of flue-dust at Great Falls, Mont., have shown that blast-furnace charges containing briquettes make a great deal more flue-dust than those that do not; also that it is more difficult to collect the values in blast-furnace dust than in the dust from the MacDougall roasting furnaces. This is brought out clearly in Fig. 251.

**124. Hearth Accretions (Sows), Etc.**—Hearth accretions are of less common occurrence in treating sulphide ores, since the internal crucible has been abandoned. An accretion consists of Fe-Cu alloy mixed with  $\text{Fe}_3\text{O}_4$ , matte, slag, perhaps some speise and other metallic compounds. The formation of a sow in treating roasted ore is probably caused by an excessive reducing effect upon the oxidized iron in the charge. In partial pyritic smelting, especially when a slag of high formation temperature is formed, causing FeS to split in part into Fe and S, the formation of a sow has probably to be attributed to the separation of Fe from matte; Fulton<sup>2</sup> believes the separation to be due in part to the reactions  $2\text{FeS} + \text{Fe}_3\text{O}_4 = 5\text{Fe} + 2\text{SO}_2$  and  $\text{FeS} + 2\text{FeO} = 3\text{Fe} + \text{SO}_2$ , but this has still to be proved. The other irregular products, such as wall accretions, furnace drawings, and refuse, need no further discussion.

**125. Results.**—The yield of metal in smelting sulphide copper ore carrying precious metal, but not contaminated with Pb and Zn, is high, as the only losses involved are those by dusting and slagging. The recovery of Cu is therefore well up in the nineties, say 97+ per cent., that of Ag 98+ per cent., and of Au 100+ per cent.

The cost of smelting in the U. S. varies within wide ranges; the lowest is probably \$0.50 per ton of charge, the highest \$3.00. Beardsley<sup>3</sup> estimates the cost at Mount Lyell to be \$2.36; at Copper Hill (Tennessee Copper Co.), \$1.24; in Mexico, \$2.03; at Granby, B. C., the same as at Copper Hill. Austin<sup>4</sup> gives for the Tennessee Copper Co., \$0.96, for the Granby Cons. M. S. & P. Co., \$1.20. The report of the Tennessee Copper Co. for 1911<sup>5</sup> gives the cost as \$0.89 per ton charge; that of Balaklala, \$3.00 per ton;<sup>6</sup> that of Cananea, \$2.571 per ton of copper-bearing material.<sup>7</sup> These figures are low when compared with the sworn data for Butte in 1901-02<sup>8</sup> which were with the Montana

<sup>1</sup> *Tr. A. I. M. E.*, 1913, XLVI.

<sup>2</sup> *Eng. Min. J.*, 1904, LXXVIII, 333.

<sup>3</sup> *Eng. Min. J.*, 1906, LXXXII, 3971.

<sup>4</sup> *Min. Sc. Press*, 1911, CII, 178.

<sup>5</sup> *Eng. Min. J.*, 1912, XCIII, 1035.

<sup>6</sup> *Eng. Min. J.*, 1912, XCIII, 937.

<sup>7</sup> *Eng. Min. J.*, 1912, XCIV, 114.

<sup>8</sup> *Eng. Min. J.*, 1903, LXXV, 708.

Ore-Purchasing Co., \$5.96 and with the Butte and Boston Cons. M. Co., \$4.84 per ton of ore. The cost in Montana today is about \$2.00 per ton charge.

As regards the smelting power of a furnace, that obtained with a reducing fusion is by far greater than with pyritic treatment.<sup>1</sup>

The rating of a furnace,<sup>2</sup> *i.e.*, the amount of charge smelted in 24 hr. per square foot of hearth area, ranges from 4 to 9 tons, the larger figure referring to roasted ore. However, a pyritic charge ought to be coarse; many plants have to deal with ore finer than desirable, and fine ore reduces tonnage. Further, the character of the slag that is being made has an important influence upon the amount of charge that can be put through. Thus it is not possible to say off-hand what ought to be the amount to be treated in a given time per square foot of hearth area, either in a reducing or a pyritic fusion.

#### 126. Production in the Blast-furnace of Metallic Copper from Matte.—

Formerly matte was brought forward to metallic copper by roasting and then smelting in the blast-furnace. This mode of procedure has become practically obsolete in the U. S., while it is still practised in other countries. Low-grade matte is enriched to converting-grade in the blast-furnace by pyritic smelting. The practice of the Tennessee Copper Co. is given in Table 28. It was found there that a 44×180-in. furnace put through more matte than ore, and that the reverse was the case with a 56×180-in. furnace; also that the 44×180-in. furnace gave a gas richer in SO<sub>2</sub> and SO<sub>3</sub> than the 56×180-in. furnace. With the matte<sup>3</sup> is mixed flue-dust. The matte, held in a car of 105 cu. ft. capacity, is poured on to a sloping yard 80 ft. long which is divided into beds 18 ft. wide.

### III. SMELTING IN THE REVERBERATORY FURNACE

#### 127. Smelting in the Reverberatory Furnace in General (Welsh Process).<sup>4</sup>—

The characteristics of matting sulphide copper in the reverberatory furnace are, that fine ore, usually rough-roasted by a separate operation, is smelted on a silica-hearth for Cu-Fe matte, with from 33 to 45 per cent. Cu, and an acid slag, with 36+ per cent. SiO<sub>2</sub>. The matte is brought forward to metallic Cu either by several steps in reverberatory furnaces or by a single operation in a converter.

<sup>1</sup> Douglas, "Power-plant of Copper Queen Smelter," *Tr. Inst. Min. Met.*, 1913; *Eng. Min. J.*, 1913, xcv, 757; *Min. Eng. World*, 1913, xxxviii, 669.

<sup>2</sup> *Eng. Min. J.*, 1903, lxxv, 442 (Van Liew), 472 (Channing), 513 (Neill, Heywood), 624, 661 (Metcalfe); Table 28.

<sup>3</sup> Guess, *Eng. Min. J.*, 1910, xc, 866.

<sup>4</sup> Le Play, "Description des Procédés Métallurgiques employés dans le pays des Galles pour la Fabrication du Cuivre," etc., *Ann. Min.*, 1848, xiii, 3, 389, 557; transl. into German by C. Hartmann, 1851, sold by Craz and Gerlach, Freiberg, Saxony.

Levy, "Note sur la Métallurgie du Cuivre par la Méthode Galloise," *Rev. Un. Min.*, 1884, xvi, 286-339; *Berg. Hüttenm. Z.*, 1885, xlv, 396, 493, 469, 485, 497, 507.

Moore, *Eng. Min. J.*, 1910, lxxxix, 1021, 1063.

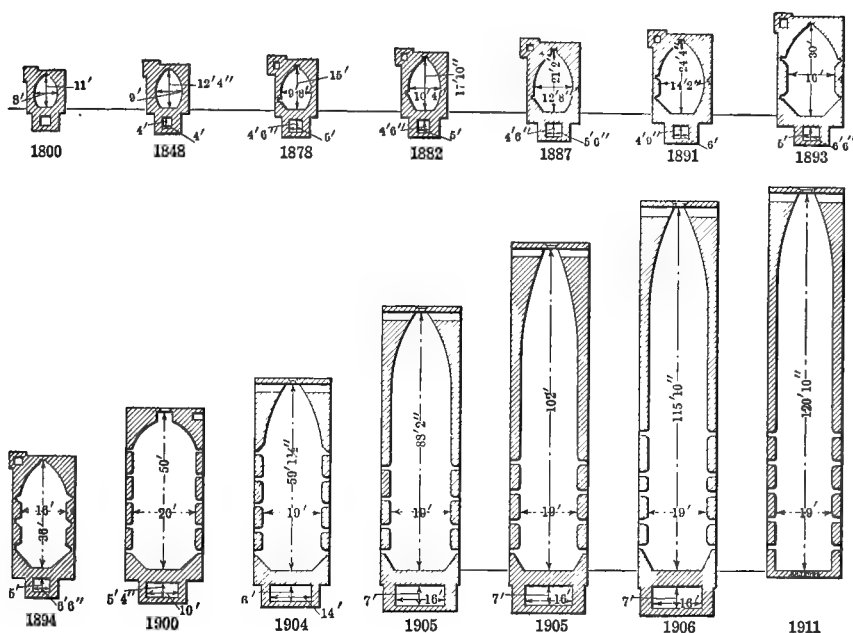
Mathewson, *Eighth Internat. Congr. Appl. Chem.*, 1912, iii, p. 113; *Tr. A. I. M. E.*, 1912, xlv, 781.

Laist, *Eighth Internat. Congr. Appl. Chem.*, 1912, iii, 97; *Tr. A. I. M. E.*, 1913, xlv, 806.

The slag goes to waste. In the reverberatory furnace S is the leading reducing agent, the carbonaceous fuel burnt serves only to furnish the heat necessary for the chemical reactions to take place between ores and fluxes.

The reverberatory-furnace charge is best made up of fine ores, hence the method of smelting is used mostly for concentrates; coarse ores, rich enough to pay for direct-smelting, usually go to the blast-furnace (comparison, see § 152) The ores are rough-roasted in fine-ore furnaces and are charged, if possible hot ( $400\text{--}500^{\circ}\text{C.}$ ), into the smelting furnace.

Reverberatory smelting of ore for matte has been developed in the United States first by Pearce in Colorado, and later by Allen, Keller, Klepetko, Mathewson, and others in Montana, so that it occupies to-day a position quite different from the early Welsh or European Continental practice. It will be therefore discussed as an independent process.



FIGS. 252-265.—Evolution of reverberatory matting furnaces.

**128. The Reverberatory Matting Furnace in General.**—The sketches given in Figs. 252-265 represent the leading stages in the development<sup>1</sup> of the non-regenerative matting furnace. An example of the regenerative type is given in detail in § 134. The figure for the year 1848 resembles the early form described by Le Play. This has a large deep fire-place, an oval concave hearth contracted slightly near the fire-bridge, very much so near the flue; there are a working-door on one side, a matte-tap on the other, and a skimming door at the

<sup>1</sup> Editor, *Min. Sc. Press*, 1910, CI, 69.  
Mathewson, *loc. cit.*

end, above which is an inclined flue leading the gases into a well-drawing stack. The hearth slopes from fire- and flue-bridges toward the center and from the back toward the front, the deepest point, at which is situated the tap-hole. As this furnace treated in 24 hr. only 8.6 tons of charge (see Table 50), it was essential that the capacity be increased, especially in the United States, if it was to compete with the blast-furnace. This was done by R. Pearce, first at Black Hawk,<sup>1</sup> and later at Argo,<sup>2</sup> Colo. The original oval form was retained from 1878 until about 1891, when one side was slightly straightened in order to furnish room for two working doors. The cast-iron rule of requiring an oval plan having been broken, the oval sides were straightened more and more and thus a gain in hearth area secured until the standard of 1900, with a hearth 20 by 50 ft., was reached. Then E. P. Mathewson increased the length of the coal-fired furnace to 102 and even 115 ft. 10 in. and with it the mode of operating. Oil-fired furnaces reached in 1911 a length of 120 ft. 10 in.; in 1913 one of 130 ft., which is probably the greatest permissible length. The leading facts of the development of the coal-fired reverberatory furnace have been brought together in Table 50.

TABLE 50.—TYPES IN DEVELOPMENT OF NON-REGENERATIVE COAL-FIRED REVERBERATORY MATTING FURNACES

Locality, date	Hearth		Grate area, sq. ft.	Chimney area, sq. ft.	Charge in 24 hrs., tons	Ratio			Coal, tons		
	Length × width, ft.	area, sq. ft.				Hearth: grate	Grate: chimney	Charge, lb. 24 hr.: 1 sq. ft. hearth	Total	Per sq. ft. grate area	Charge, tons, per ton coal
Wales, 1848.....	14×10	120	20	4.66	8.6	6:1	4.3:1	144	11.2	0.56	0.77
Colorado and Montana, 1891.	24×14	265	28.5	9	28	9.3:1	3.17:1	211	10	0.36	2.80
Anaconda, Montana, 1900.	50×20	886	53.3	30.68	105	16.6:1	1.73:1	236	35	0.66	3.03
Anaconda, Montana, 1906.	112×19	1,985	112	?	300	17.7:1	?	302	62.5	0.55	4.8

**129. The Reverberatory Furnace in Detail.**—Modern reverberatory furnaces, Figs. 252–265, show much similarity in their general form. A few typical forms have been selected for the discussion of the construction; the modes of firing with lump coal, fuel dust, oil, and producer gas; and the management; they are the furnaces of the Colorado Smelting Co., Butte, Mont., 1903; of the Anaconda Copper Mining Co., Anaconda, Mont., 1908; the Canadian Copper Co., Copper Cliff, Ont., 1912; the Cananea Consolidated Copper Co., Cananea, Sonora, Mex., 1912; and the Anaconda Copper Mining Co., Great Falls, Mont., 1912.

**130. Furnace of the Colorado Smelting Co., Butte, Mont., 1903.**—This is shown in Figs. 266–271. It has a hearth 49 ft. 6 in. by 20 ft. 2 in. which has air-flues underneath to cool the bottom and to furnish preheated air to a box on the

<sup>1</sup> Egleston, *Tr. A. I. M. E.*, 1875–76, IV, 276.

<sup>2</sup> Pearce, *Tr. A. I. M. E.*, 1889–90, XVIII, 55.

roof above the fire-bridge, whence the air enters the furnace and assists the combustion of the fire-gases. The furnace, dismantled several years ago, served to produce high-grade matte which was tapped at intervals into a series of communicating cast-iron molds and shipped to Argo, Colo., for further treatment. The ground-plan, Fig. 266, gives the rock and brick foundation-walls with the ash-pit floor of the fire-place at one end and the base of the stack at the other. Cold air is forced in at this level; it enters through flue *a*, passes around partition-wall *b*, returns by flue *c*, and travels along vault *d*. Following it in Figs. 269 and 267, it rises 25 ft. in two corners, *e*, of the stack (square on the outside, circular on the inside), to descend in the others, *e'*, when it is divided by tongue *f*, Fig. 267, into branches *g* and *h*; branch *g* furnishes the air for flues  $g_1 g_2 g_3$ , while branch *h* supplies it to flues  $h_1 h_2 h_3$ . Arriving at the fire-bridge end of the furnace, the

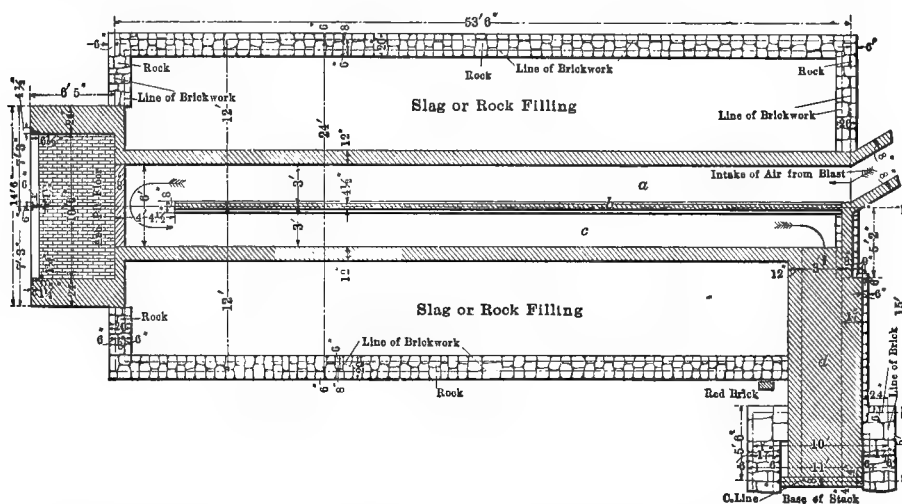
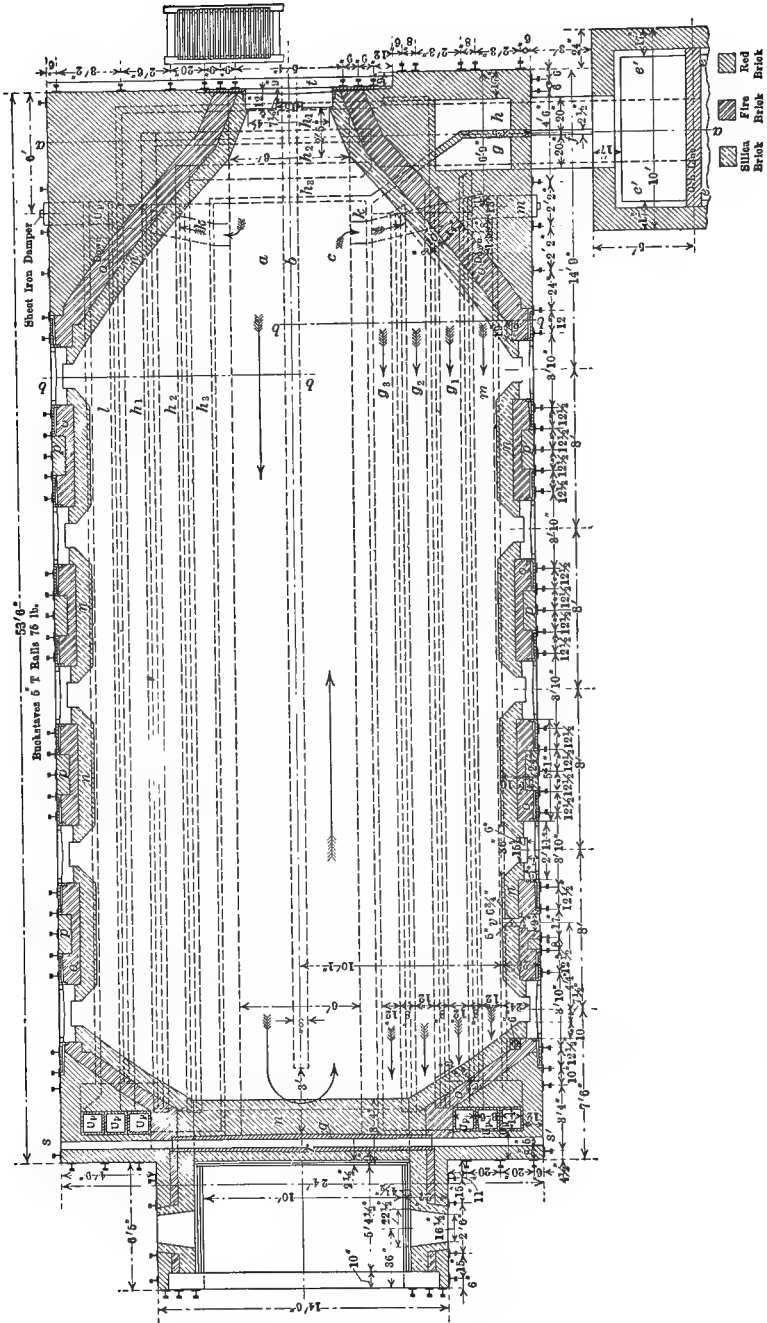


FIG. 266.—Reverberatory matting furnace Colorado Smelting Co., ground plan.

heated air rises in corresponding vertical flues, enters the air-box *i*, Fig. 269, and descends through ports, *j*, situated in the roof above the fire-bridge wall. In Fig. 267 there are indicated branch-inlets *K* and *K'* from flues *a* and *c* which communicate with longitudinal channels *l* and *m*; they serve to control the temperature of the air passing through  $g_{1-3}$  and  $h_{1-3}$ , and are regulated by sliding dampers *l'* and *m'*. Turning to Figs. 267 and 268, the inner side-walls, *n*, of the hearth are of silica-brick backed by fire-brick, *o*, which in their turn are replaced by red brick, *p*, wherever possible. The roof, always made of silica-brick 15-18 in. long, has five charging-ports, the inner sides of the fire-place are also of silica-brick. The fire-bridge air-space is enclosed by two heavy cast-iron plates, the bridge-plate *q* and the E-shaped casting *r*; beneath the skimming-door is placed the front-plate *t*; both serve to distribute the longitudinal thrust evenly upon the buckstays.

In smaller furnaces the bridge-plate, extending beyond the fire-bridge to the





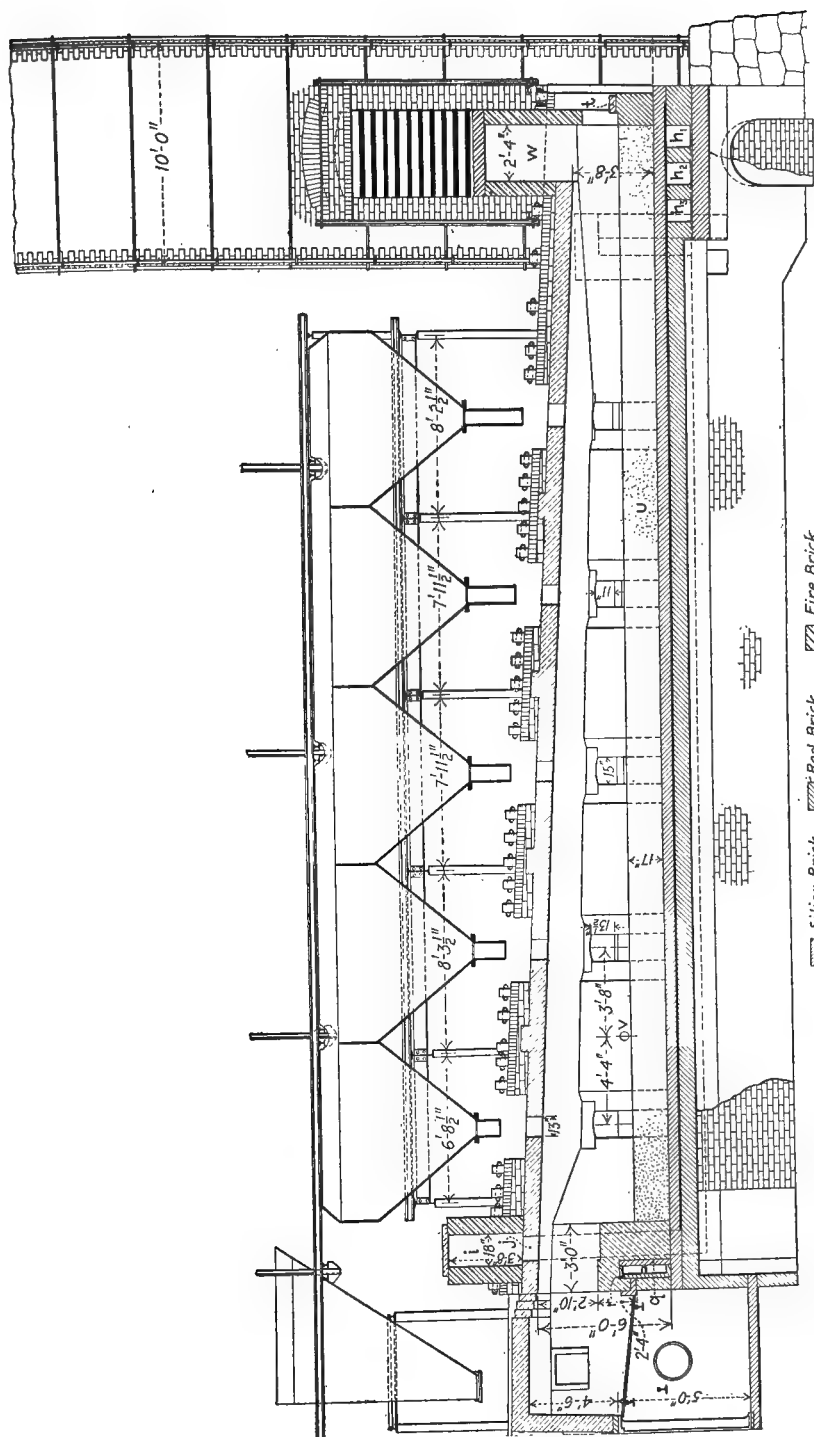


FIG. 268.—Reverberatory matting furnace, Colorado Smelting Co., vertical longitudinal section.



points  $s$  and  $s_1$  (Fig. 267) and forming parts of the end-wall, is called conker-plate;<sup>1</sup> the buckstays are placed against conker- and front-plates.

The putting-in of the working bottom is taken up in § 139. The tap-hole  $v$  is placed on the side near the fire-bridge between the first and second doors. With a grate 10 ft. long, it is necessary to have a fire-door on either side to permit successful grating. The fire-place receives its coal through an opening in the roof fed from a hopper; it is run with undergrate blast. The fire-gases leave the furnace through a short inclined flue,  $w$ , Fig. 269, ending in a small dust-chamber,  $x$ , and then pass into the stack. Flue  $w$  is covered with tiles clamped with heavy channels. The work of the furnace is given in Table 51.

The furnace of the Anaconda Co. of 1903, at Anaconda,<sup>2</sup> had the same general form as that of the Colorado Smelting Co., only the waste heat was utilized<sup>3</sup> by passing the gases through a 300-h.p. Stirling boiler.<sup>4</sup> The draft should not be less than 1.7 in. water.

Clark<sup>5</sup> published recently a drawing of a modern small-size reverberatory matting furnace.

Nearly all reverberatory smelting plants have followed the example set by Anaconda of using Stirling waste-heat boilers. Sørensen<sup>6</sup> compared the Stirling with the Babcock & Wilcox boiler at the works of the Nevada Consolidated smeltery, where they were in operation, and came to the conclusion that the cost of cleaning in the Stirling is much less than with the Babcock & Wilcox, and that the evaporative power of the Babcock & Wilcox greatly exceeds that of the Stirling; in fact, 1 lb. of oil burned in the reverberatory matting furnace evaporates only 3.315 lb. water in the Stirling as against 7.91 lb. in the Babcock & Wilcox, and this more than compensates for the extra cost and the time lost in cleaning and repairing.

**131. Furnace of the Anaconda Copper Mining Co., Anaconda, Mont., 1908.**<sup>7</sup>—This furnace designed by E. P. Mathewson is shown in Figs. 272–274. The hearth is 111 ft. 8 in. long; its sides are parallel for a distance of 74 ft.; the enlargement from the fire-bridge (length 16 ft.) to normal width of 19 ft. is abrupt, the contraction from 19 ft. toward the flue-end to 7 ft. is gradual, taking up 32 ft. of the length of the furnace. A right degree of contraction is one of the essentials for obtaining a temperature sufficiently high to keep the slag fluid at the flue-end. The bottom is built up solid of slag, 24 in. deep, poured hot, and covered by 12 in. of silica brickbats.

The earlier practice of having a concrete foundation has been abandoned, as

<sup>1</sup> Barbour, Conker-plate details, *Eng. Min. J.*, 1912, XCIV, 541.

<sup>2</sup> Drawing, *Min. Ind.*, 1902, XI, 202; Work, Table 41.

<sup>3</sup> Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 295.

<sup>4</sup> Waste-heat boiler of the Colusa-Parrot M. & S. Co., Butte, Mont., *Eng. Record*, 1907, LVI, 11.

<sup>5</sup> *Min. Sc. Press*, 1910, C, 579.

<sup>6</sup> *Min. Sc. Press*, 1913, CVII, 575.

<sup>7</sup> Austin, *Tr. A. I. M. E.*, 1906, XXXVII, 468.

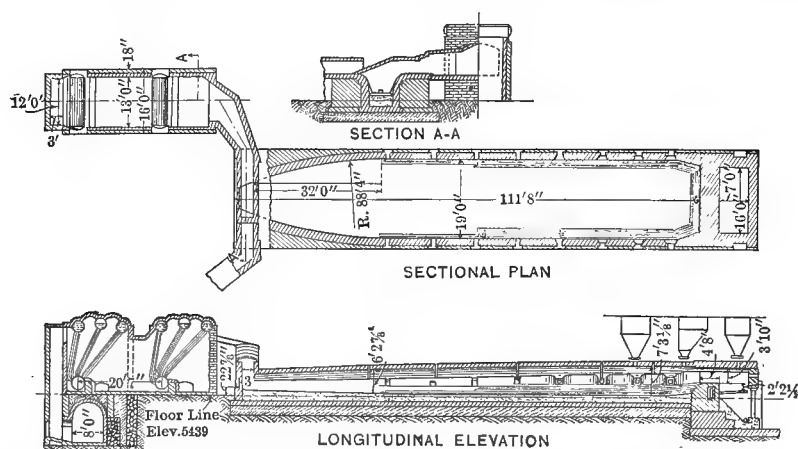
Offerhaus, *Eng. Min. J.*, 1908, LXXXV, 1234; Detail Drawing.

Mathewson, *Tr. A. I. M. E.*, 1912, XLIV, 781.

on penetration of the heat, the concrete has tendency to rise and affects unfavorably the silica bottom.

The omission of underground flues, shown in Fig. 266-271 and formerly deemed necessary, is now characteristic for most large reverberatory furnaces which treat ore and store considerable amounts of matte going direct to converters; the principle followed is to make the bottom strong and to keep it hot; air cooling still prevails with matting and copper-refining furnaces which are tapped at short intervals when enough matte has been accumulated, or the copper is ready for molding.

The parallel sides of the furnace have ten working doors,  $8 \times 15$  in., the sills of which are 18 in. above the skimming plate at the flue-end. The roof, made of  $15 \times 6 \times 3$ -in. silica-brick, has near the fire-bridge only four feed-openings for ore, as the mode of charging differs from that of the older furnaces, and four



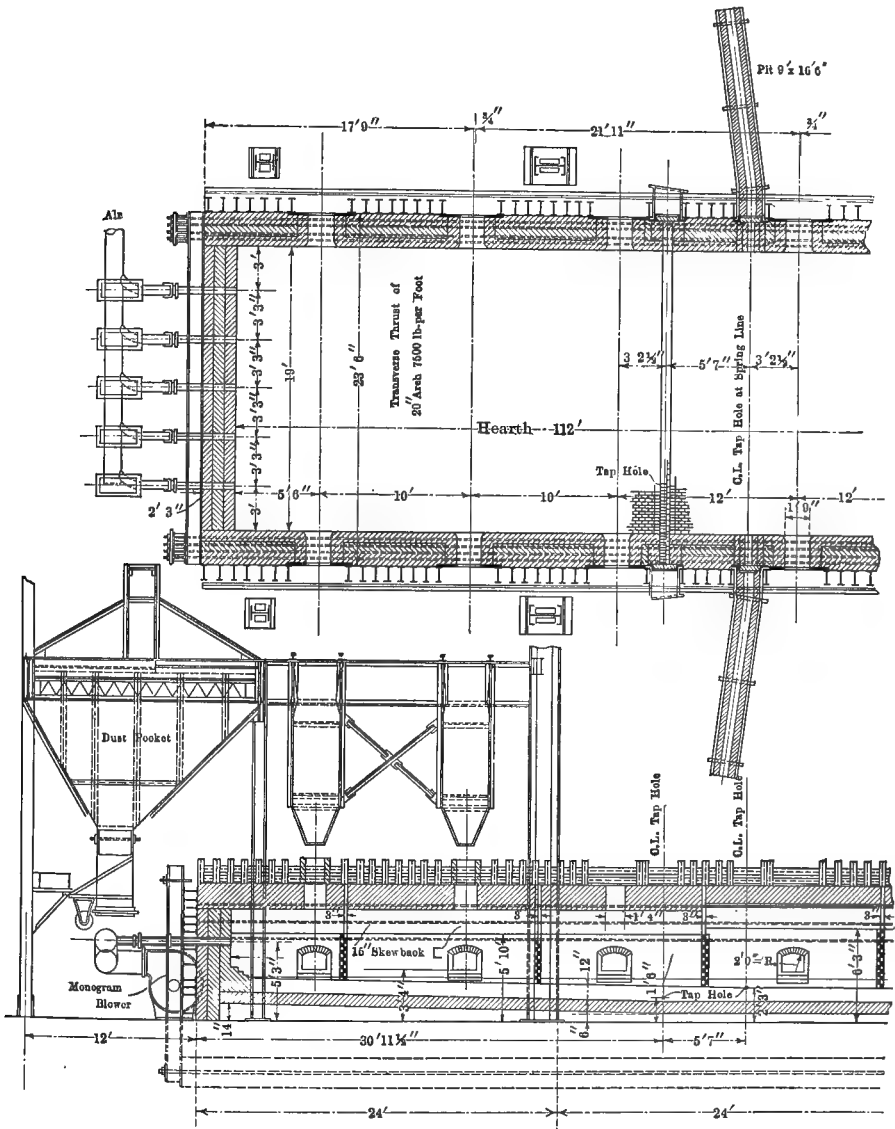
FIGS. 272-274.—Reverberatory matting furnace and boilers, Anaconda, Montana.

ports, 12 in. sq., for coal. There are twenty  $3 \times 3$ -in. holes in the roof above the fire-bridge for the admission of air to assist in the combustion of the fire-gases. An expansion-space of  $\frac{1}{4}$  in. to running foot is provided for by the introduction of cardboard. In the front wall of the fire-box are two circular openings, 12 in. in diameter, closed by wheel-doors, which serve to ascertain the height of the bed of coal on the grate. The furnace is ironed by 8-in. 18-lb. I-beams tied only at the tops by 2-in. rods, the bottoms being secured in the foundation. The waste heat of the gases is utilized by two 300-h.p. Stirling boilers placed in series; the gases leave the hearth at a temperature of  $1100^{\circ}\text{C}$ ., enter the tubes at  $950^{\circ}\text{C}$ . and issue from them at  $330^{\circ}\text{C}$ .; the draft ranges from 1.7 to 2.0 in. water. The results attained are given in Table 41; the mode of operating is discussed in § 149.

The coal-fired furnaces at Garfield<sup>1</sup> and especially the oil-fired furnaces have economizers between the boilers and the stack.

<sup>1</sup> *Eng. Min. J.*, 1911, XCI, 752.

132. Furnace of the Canadian Copper Mining Co., Copper Cliff, Ont.,<sup>1</sup> 1912.  
—The firing end of this furnace is shown in horizontal and vertical longitudinal



FIGS. 275-276.—Reverberatory matting furnace, Canadian Copper Co., firing-end.

sections in Figs. 275 and 276, the flue-end in Fig. 277, and some detail of the side wall in Fig. 278. The leading points wherein the furnace differs from others

<sup>1</sup> Browne, *Tr. Canad. Inst. Min. Eng.*, 1912, xv, 114; Private Notes, 1912.

are, that the working hearth is of magnesite brick; that the inner sides are of the same material excepting at the slag-level, where it is replaced by chrome brick; and that it is fired with fuel-dust.

The hearth is 112 by 19 ft., has parallel sides for a distance of 83 ft. 3 in., which then contract in a distance of 28 ft. 9 in. to 7 ft. 9 in. The inner height at the firing end is 6 ft.; there are nine doors on a side distributed over the parallel sides; the side walls are 27 in. thick, of which 18 in. are of silica-brick supporting the roof; inside of the silica-brick is a 9-in. course of magnesite brick with chrome brick at the slag level, Fig. 278. The roof of silica-brick is 20 in. thick for the first 35 ft. near the burners, and 15 in. for the remainder of the way. The hearth of magnesite brick slopes from the ends to the lowest point, which is

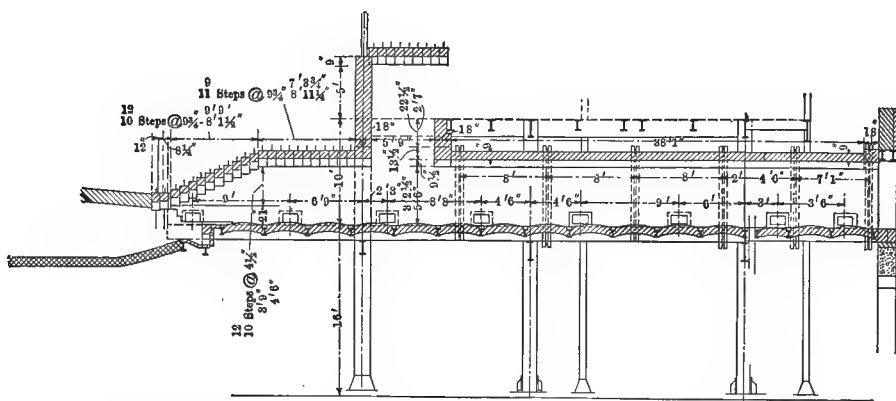


FIG. 277.—Reverberatory matting furnace, Canadian Copper Co., flue-end.

28 ft. 8½ in. distant from the burners; here is placed one matte tap 12 in. above the floor, and 5 ft. 7 in. nearer the burners a second, flush with the bottom. On either side of the furnace near the matte taps is an in-pour for converter slag arriving in a tunnel, through which also the matte is hauled to the converters; flue-dust, mixed with green-ore fines, is charged through two hoppers in the roof which discharge along the center line of the furnace. The waste slag is removed from both sides about 11 ft. from the point at which the side walls begin to converge.

The foundation for the working hearth is of slag, 2 ft. deep, poured into place between the outer walls and shaped to the form of an inverted arch with a spring of 12 in. On this are placed a 2½-in. course of fire-brick, and then a 9-in. course of magnesite brick laid with a mortar of ground magnesite and linseed oil; an expansion space of ¼ in. to the foot is allowed for by using wooden strips, ¼ in thick, every six courses, and having them staggered. The firing is taken up in § 142.

The throat through which the gases leave the furnace is about 27 feet square. They pass, Fig. 277, into a cross-over flue, 6 by 9 ft. and covered by cramps, lead-

ing into the main dust flues (15 by 19 by 177 ft.) of the two reverberatories, which is connected with the stack 200 ft. high, 17 ft. 2 in. in diameter at the bottom and 15 ft. 4 in. at the top. Very little dust is collected in the chamber. There are charged hourly about 10 tons of flue-dust with green-ore fines and 16 tons of converter slag; the coal is shut off when dust is fed, and this is allowed to drop from the feed-hopper until it ceases to float off on the slag. The flame is about 100 ft. long, the temperature at the fire-end is  $1550^{\circ}\text{C.}$ , at the skimming-

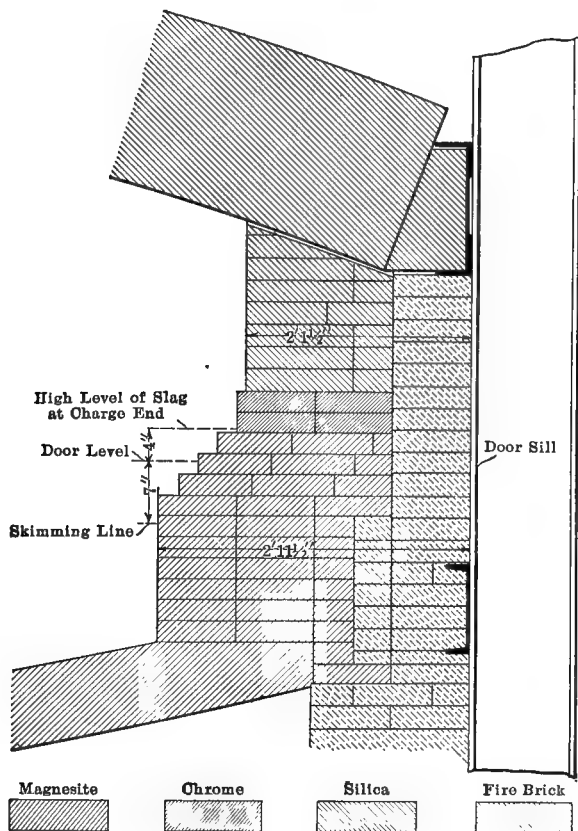


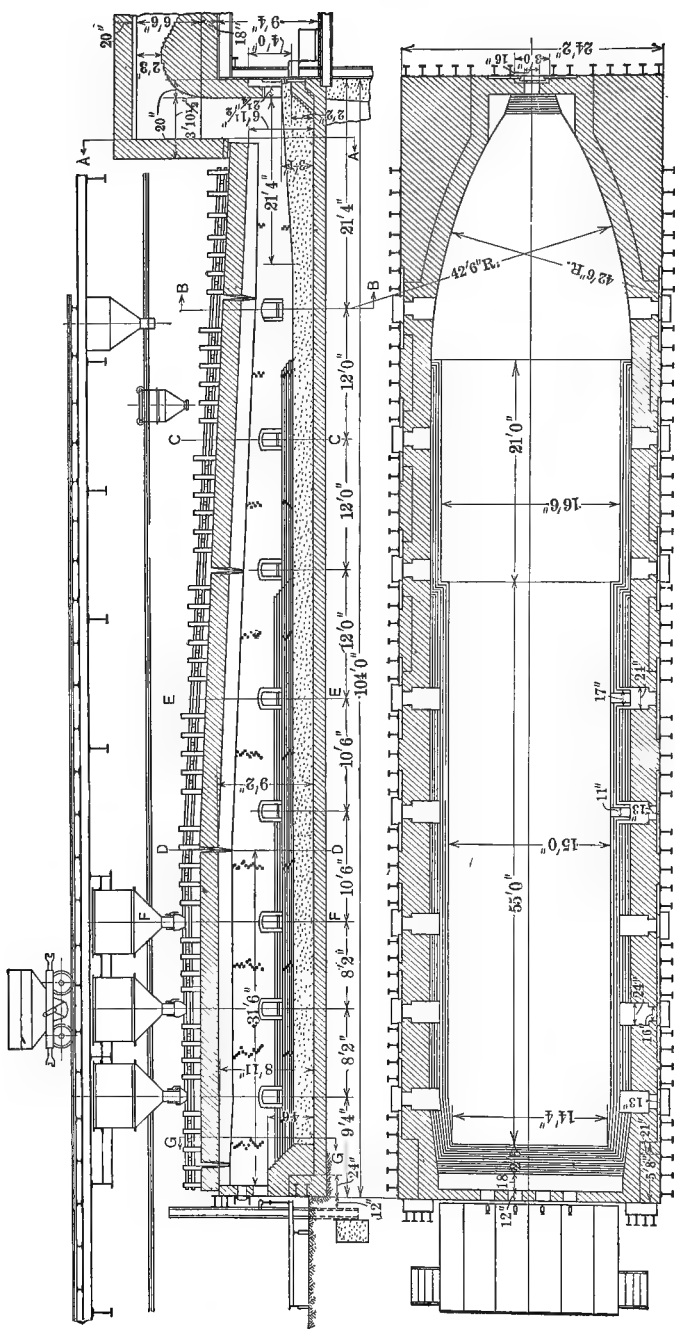
FIG. 278.—Reverberatory matting furnace, Canadian Copper Co., bricking of side-wall.

door  $980^{\circ}$  and in the stack  $500^{\circ}\text{C.}$  Fine ore is used as fettling. Two furnaces treat in 24 hr. about 400 tons of converter slag and 125 tons of flue-dust. Data are given in Table 51.

**133. Furnace of the Cananea Consolidated Copper Co.,<sup>1</sup> Cananea, Sonora, Mexico.**—This furnace, fired with oil, is shown in Figs. 279–287. General data

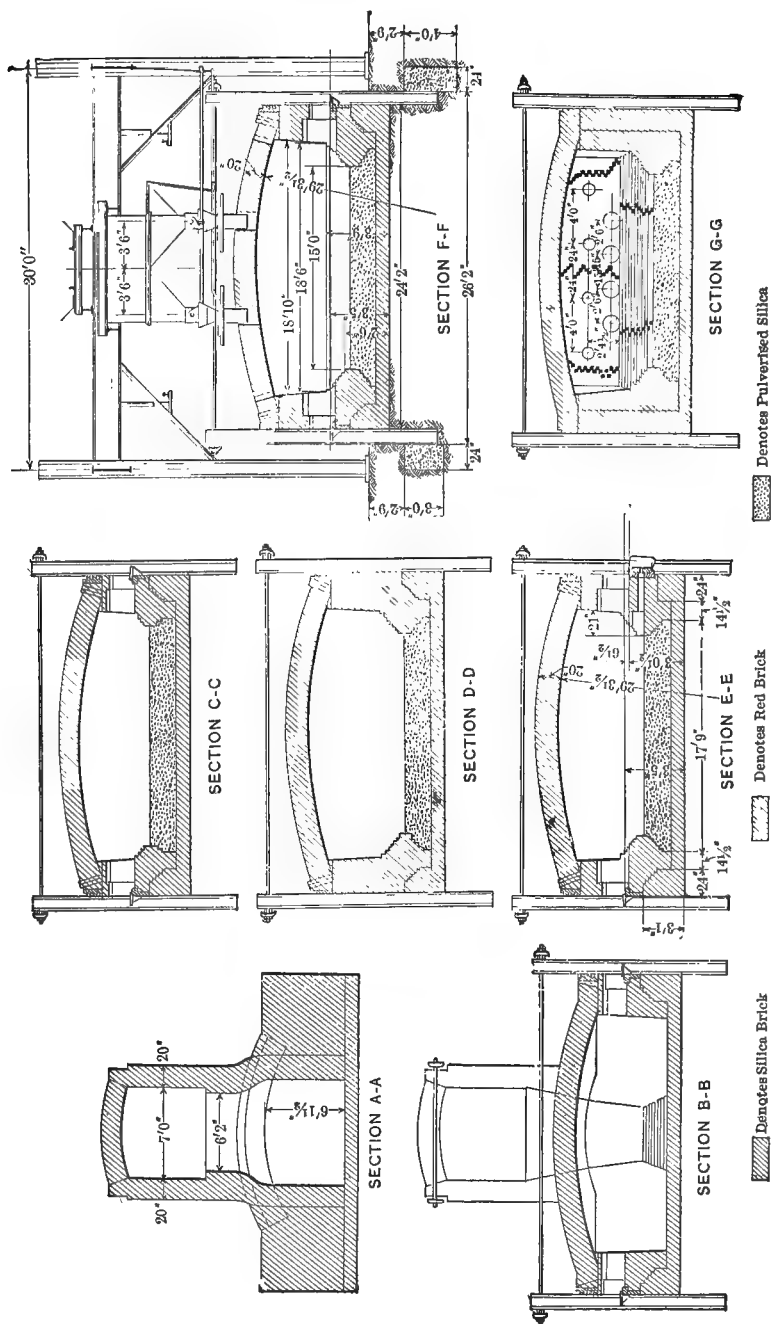
<sup>1</sup> Ricketts, *Tr. Inst. Min. Met.*, 1909–10, XIX, 147; *Eng. Min. J.*, 1910, LXXXIX, 315, 404 (Heywood), 619 (Collins), 827 (Grabill), 959 (Gormly), 1021, 1063 (Moore); 1911, XCII, 693.

Mathewson, *Tr. A. I. M. E.*, 1912, XLIV, 781.

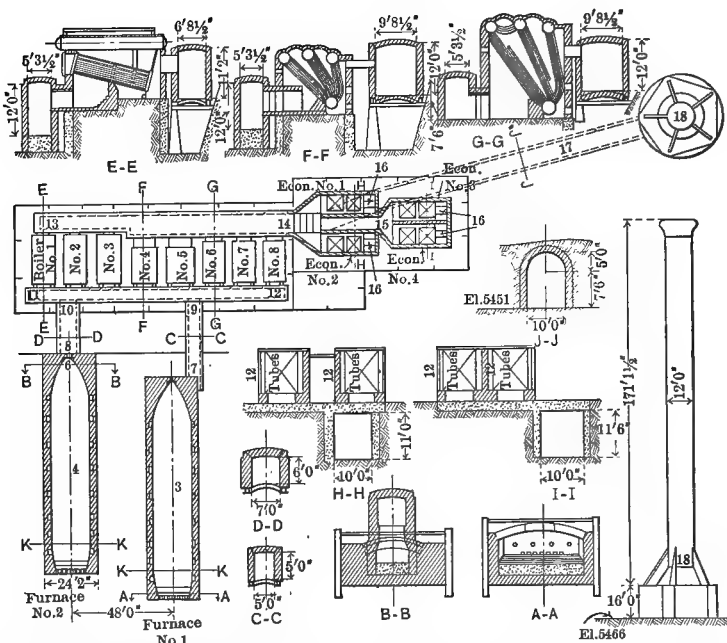


FIGS. 279-280.—Oil-fired reverberatory matting furnace, Cananea.





FIGS. 281-287.—Oil-fired reverberatory matting furnace, Cananea.



FIGS. 288-301.—General data of oil-fired reverberatory matting furnace, Cananea.

## General Data.

	Area, Sq. Ft.	Area, Sq. Ft.
Two reverberatory furnaces, 100 by 19 ft.		
Hearth, K. K.		
Seven burner-holes, 6 by 10 in.	3	
Four peep-holes, 10-in. diameter	2	
Throat of furnace No. 1, 5 ft. wide, 2 ft. 8 in. high	14	
Throat of furnace No. 2, 7 ft. wide, 1 ft. 9 in. high	14	
Furnaces Nos. 1 and 2, throats	28	
Cross-over flue No. 1, 5 ft. wide, 5 ft. high, 50 ft. long	28	
Cross-over flue No. 2, 7 ft. wide, 6 ft. high, 27 ft. long	44	
Flue to boiler at 11	60	
Flue to boiler at 12	40	
Flue from boilers at 13	76	
Flue from boilers at 14	120	
Boiler No. 1, area entering, 34 sq. ft.; leaving	18	
Boiler No. 2, area entering, 34 sq. ft.; leaving	18	
Boiler No. 3, area entering, 34 sq. ft.; leaving	18	
Boiler No. 4, area entering, 38 sq. ft.; leaving	20	
Boiler No. 5, area entering, 38 sq. ft.; leaving	20	
Boiler No. 6, area entering, 30 sq. ft.; leaving	19	
Boiler No. 7, area entering, 30 sq. ft.; leaving	19	
Boiler No. 8, area entering, 30 sq. ft.; leaving	19	
Boilers, Total area entering, 288 sq. ft.; leaving	151	
Boilers Nos. 1, 2, 3, Aultmann & Taylor, 250 h.-p., each		
Boilers Nos. 4 and 5, Stirling, 250 h.-p., each		
Boilers Nos. 6, 7, 8, Stirling, 300-h.-p., each		
Economizer No. 1, area entering, 83 sq. ft.; leaving	45	
Economizer No. 2, area entering, 83 sq. ft.; leaving	45	
Economizer No. 3, area entering, 83 sq. ft.; leaving	45	
Economizer No. 4, area entering, 83 sq. ft.; leaving	45	
Underground flue	115	
Stack, 12 ft. 6 in., 17 1/2 ft. 1 1/2 in. high, base	123	
Smallest area for passing gases, 14 sq. ft.; largest area	123	
California crude oil used, S. G., 0.966		
Weight per barrel of 42 gal., 330 lb.		
Heat-content per lb., 18,700 B.t.u.		
Economizers, Green Economizer Co., 288 tubes		
Seven oil-burners per furnace, 0.43 lb. of steam required to atomize 1 lb. of oil		
Total travel of gases in furnace No. 1	690 ft.	
Total travel of gases in furnace No. 2	730 ft.	
Draft.		
Temperature of gases at 9 and 10, 2,300°		
2,400° F.	0.25	
Temperature of gases at 14, 500° F.	0.60	
Temperature of gases at 18, 350° F.	0.90	

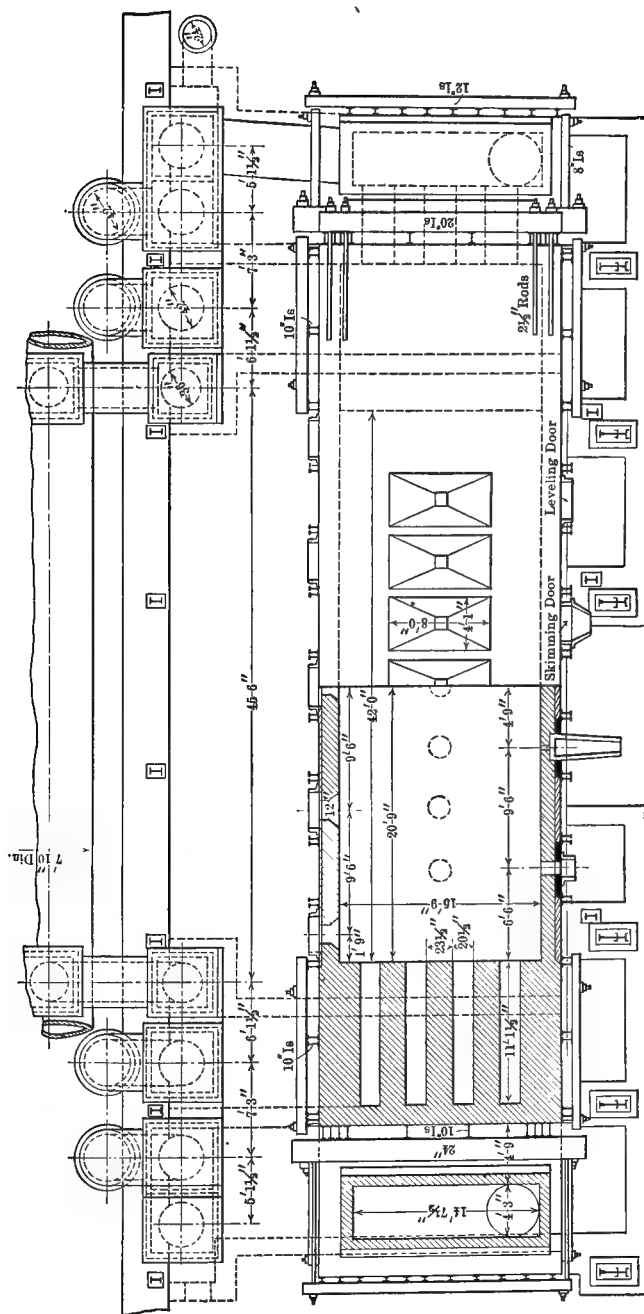


FIG. 302.—Gas-fired reverberatory matting furnace, Great Falls.

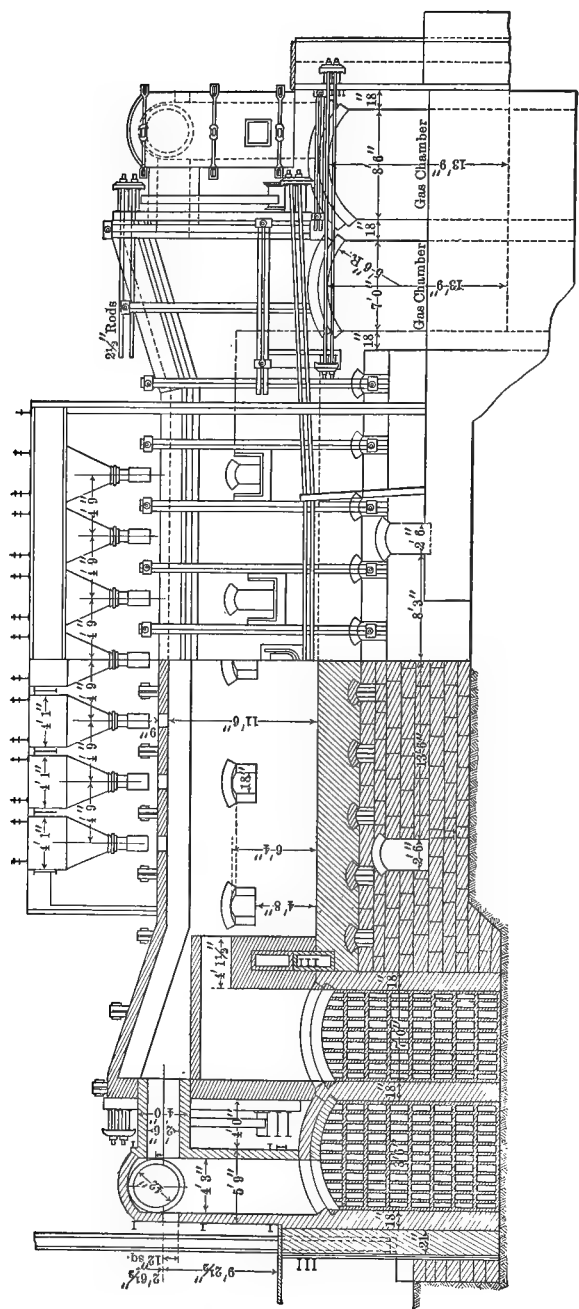
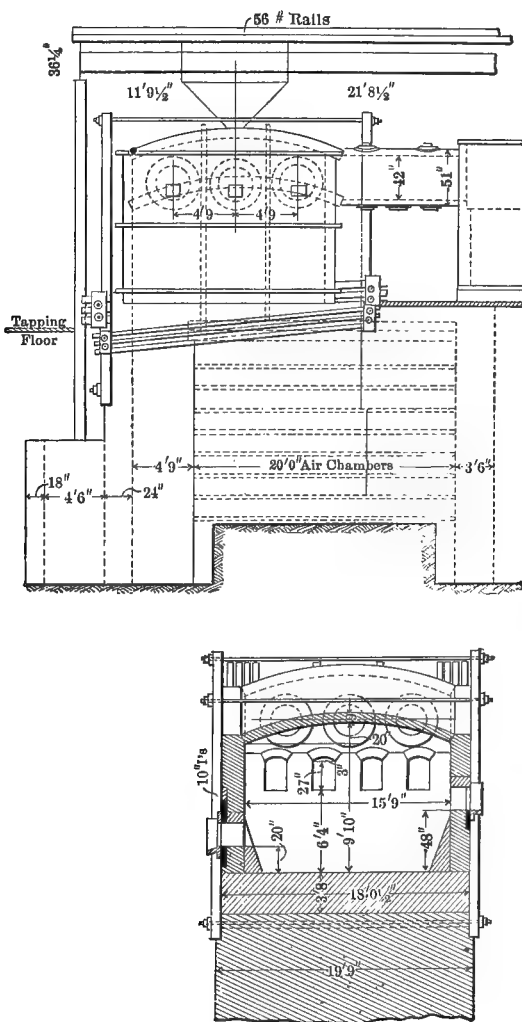


FIG. 303.—Gas-fired reverberatory matting furnace, Great Falls.

are assembled with Figs. 288-301. The hearth, 100 by 19 ft., is contracted comparatively rapidly at the flue-end. At the opposite end are the openings for four oil-burners. The six ore-hoppers originally used have recently been reduced to three. The inner parts of the hearth are of silica-brick. The fire-gases pass



FIGS. 304-305.—Gas-fired reverberatory matting furnace, Great Falls.

in parallel through two 300-h.p. Stirling boilers; there is no by-pass. Crediting the furnace with 0.464 bbl. oil for steam raised in the waste-heat boilers, the total oil consumed per ton of ore of 1.121 bbl., given in Table 51, is reduced to 0.657 bbl.

**134. Furnace of the Anaconda Copper Mining Co., Great Falls, Mont.**<sup>1</sup>—This furnace fired with producer gas and provided with regenerative chambers, is shown in Figs. 302–305, selected from the ten published by Mathewson.<sup>2</sup> It has a hearth 42 ft. 6 in. long by 15 ft. 9 in. wide, which is rectangular, Fig. 302; this gives it a larger hearth-area than if the sides are tapered at the ends, but is accompanied by the drawback that the sides tend to bulge inwardly instead of outwardly as is the case with oval side-lines. The furnace is built in five sections in order to allow for expansion amounting to 14 in. over all. The sections are separate in the roof; in the side walls the necessary spaces are left open between the bricks. The roof, 9 and 12 in. thick, is of silica-brick; the sides, 18 in. thick, are of fire-brick. The upper tie-rods, Fig. 303, 1.5 in. in diameter, pass 1 ft. above the roof, as this rises as much as 9 in. when hot; the lower tie-rods pass through open flues, 2 ft. 6 in. by 3 ft. 8 in., and are thus kept cool. The checker work, Fig. 303, at either end of the furnace has a special construction to permit cleaning and thus to reduce the slagging of the checker-brick by ore-dust. The fire-brick flues in the checkers are horizontal, 18 in. high by 7 in. wide and 11 to 21 ft. long, according to position. The 9-in. brick forming the tops and bottoms of the flues are laid 4.5 in. apart in order to leave open spaces for the dust to fall through and collect in the pit at the bottom, 4 to 5 ft. deep, whence it is removed periodically. The air-chambers, Fig. 303, are 8 ft. 6 in. by 14 ft. 7½ in. and 13 ft. 9 in. high, and have each, including the exposed end-walls, a heating surface of 4900 sq. ft.; the gas chambers are 7 ft. by 14 ft. 7½ in. and 13 ft. 5 in. high, each with a heating surface of 4200 sq. ft. The air, Fig. 304, enters the hearth through a single port, 15 ft. 9 in. by 2 ft. next to the roof; the gas through four ports, 20.25 by 30 in., beneath. The products of combustion from the furnace descend in a chamber, Fig. 302, at one end of the checkers, pass through these and ascend at the opposite end. The life of the checkers is about three months. It can be increased by allowing the gases to travel during the charging-period through a by-pass direct into the main flue and thus prevent the dust from settling in the checker-flues. In the roof of the furnace are seven openings through which the charge, mainly hot calcines, is dropped into the furnace from corresponding hoppers. The end-hoppers are first emptied in order that the charge may flow toward the center, then follow the central hopper and its two neighbors, and lastly the two remaining, the flow being regulated by gates in order to insure an even distribution. In the middle of one of the sides, Figs. 302 and 305, is a spout for tapping slag, which is granulated, and matte, which is collected in ladles and transferred to the converting department. Close to this spout is a tap-hole, Figs. 302 and 304, serving to remove the total liquid content of the hearth. In Figs. 303 and 305 are seen three ports leading into the air-flue. Fig. 302 shows the positions, of the gas-flue bringing the gas (CO<sub>2</sub> 9.4, CO 16.8, CH<sub>4</sub> 2.9, H 13.3, N 57.6 per cent. vol.) from six producers gasifying together in 24 hr. from 60 to 75 tons of bituminous coal (H<sub>2</sub>O 4–6, Vol. H–C

<sup>1</sup> Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 258.

Mathewson, *op. cit.*, 1912, XLIV, 781.

<sup>2</sup> *Loc cit.*

21-27, F.C. 48-53, Ash 19-33 per cent.); of the air-flue, connected with a blower; and of both the gas- and air-reversing valves. The work done with this furnace is given in Tables 41-42.

Practical experience has shown that the surfaces of the regenerators are much too small. In the new smelter at Great Falls which is to replace the present one, each furnace will have its own gas-producer, fed and cleaned mechanically; the heat of fire-gases will be utilized in recuperators.

The predecessors of the present stationary furnaces were tilting furnaces, erected in 1890 and 1892, which were similar to the Campbell open-hearth steel furnace. They were abandoned on account of their small capacities (hearth 16 by 13 ft.) and because of the fact that it was impossible, in pouring slag, to control the flow in such a manner as to prevent matte from flowing off with the slag.

**135. Other Furnaces.**—The leading facts about other furnaces are given in Tables 51 and 52. Drawings of other modern furnaces have been published by Mathewson.<sup>1</sup>

The furnace at the Peyton Chemical Works, San Francisco,<sup>2</sup> is an oil-fired furnace with regenerators for preheating the air, an arrangement which has much to commend it.

In recent years a few special furnaces of passing importance have been put on the market, such as the Fink smelter,<sup>3</sup> the Cotton furnace,<sup>4</sup> the Brown furnace,<sup>5</sup> and the Dawson furnace.<sup>6</sup>

Examples of the older reverberatory furnaces have been tabulated by Howe.<sup>7</sup>

**136. Accessory Apparatus.**—The accessory apparatus for the collection and disposal of slag (§ 95) and matte (§ 96) are the same as with the blast-furnace. The recovery of flue-dust (§ 122) is also similar; its disposal (§ 123) differs in that it can be readily worked with the ore-charge. In fact, the reverberatory furnace often serves to work with its ore-charges the flue-dust produced by roasting and blast-furnaces.

**137. Dimensions and Working Data of Reverberatory Furnaces.**—The dimensions and work of the above reverberatory furnaces and some others are assembled in Tables 51 and 52. Table 51 had been prepared by the author when Table 52 was published by E. P. Mathewson. Both are given, as they treat the subject from different aspects; they supplement one another, even if there is some duplication.

<sup>1</sup> *Loc cit.*

<sup>2</sup> Leas, *Eng. Min. J.*, 1908 LXXXVI, 898; Pacific Foundry Co., San Francisco.

<sup>3</sup> Carter, *Technical Work Mag.*, 1909, XI, 194.

Traphagen, *West. Chem. and Met.*, 1909, V, 172.

Fink, *London Min. J.*, 1909, LXXXV, 237; *Electrochem. and Met. Ind.*, 1909, VII, 287; *Mines and Methods*, 1912, IV, 63; *Min. Eng. World*, 1912, XXXVII, 795.

Neill, *Min. Sc. Press*, 1909, XCVIII, 300.

Pulsifer, *Min. Eng. World*, 1913, XXXVIII, 952.

<sup>4</sup> Editor, *West Chem. and Met.*, 1909, V, 325.

<sup>5</sup> *Mines and Methods*, 1911, II, 167.

<sup>6</sup> *Min. World*, 1911, XXXIV, 691.

<sup>7</sup> *Bulletin* No. 26, U. S. Geol. Surv., Washington, 1885, p. 40.

TABLE 51.—REVERBER

Item	Coal-fired					
	Wales, 1848	Butte & Boston, 1903	Anaconda, 1903	Colorado S. Co., 1903	Butte Red. W'ks., 1903	Boston & Montana, 1903
Length of hearth.....	13'	50'	50'	49' 6"	50'	42' 6"
Length "a" of bridge-section.....	6'	6'	6'	4' 6"	6'	42' 6"
Length "b" of middle-section.....	28'	32'	32'	32'	32'	42' 6"
Length "c" of flue-section.....	16'	12'	12'	13'	12'	42' 6"
Width "d" of hearth at bridge.....	7' 4 1/2"	10'	10'	10' 9"	10' 9"	15' 9"
Width "e" of hearth at middle.....	8' 11"	20'	20'	20' 2"	20'	15' 9"
Width "f" of hearth at flue.....	2' 3 1/2"	4'	6'	4'	4'	15' 9"
Hearth area, sq. ft.....	120	842	886	878	878	688
Hearth thickness.....	18"	22"	24"	19"	20"	28"
Length of grate—Burners, No.....	4' 8"	10'	10'	7'	10' 9"	
Width of grate—Burners, diam., in..	4' 3 1/2"	5' 5 1/2"	5' 4"	5' 6"	5'	
Depth of grate below top of bridge at bridge—Air, cu. ft. per min.	3' 11"	1' 10"	2' 9 1/2"	2' 4"	2' 8"	
Depth of grate below top of bridge at opposite end—Air, pressure, lb.	3' 5"	1' 2"	2' 6 1/2"	1' 4"	2' 2"	
Grate area, sq. ft.....	20	53.9	53.3	53.0	53.75	Producer gas regen. chamber
Ratio, hearth to grate area.....	6:1	15.6:1	16.6:1	16.5:1	16.3:1	
Height of roof above bridge.....	1' 7 1/2"	2' 7"	2' 6 1/2"	2' 10"	2' 8 1/2"	24"
Height of roof above hearth at bridge.	3'	4' 8"	4' 4"	4' 4"	4' 8"	7' 0"
Height of roof above hearth at flue..	1' 4 1/2"	2' 1 1/2"	2' 10"	3' 0"	2' 2"	
Width of bridge.....	2' 6"	3' 0"	3' 5 1/2"	3' 0"	3' 0"	4' 1 1/2"
Size of flue at vulcatory or verb.....	15"×?	6"×30"	6"×30"	5"×30"	6"×30"	
Size of flue leading to chimney.....	22"×?	30"×48"	30"×30"	28"×30"	30"×30"	42" dia. at each end
Chimney, inside diameter.....	2' 2 1/2"	5' 6"	6' 3"	6' 0"	6' 1"	
Chimney height.....	46' 7 1/2"	70'		70'	75' 3 1/2"	
Charge, tons.....	1.43	25	15	24	18	35
Charge, time of melting, hr.....	4.3	5	3 1/2	6 1/2	4 1/2	6
Charge, tons in 24 hr.....	8.6	112.5	105	90	90	150
Charge, tons per sq. ft. of hearth in 24 hr.	0.071	0.129	0.118	0.102	0.102	0.218
Ratio of concentration.....	3:1	5.7:1	4.7:1	7.56:1	5:1	3 1/2:1
Fuel, bituminous coal, manner of firing, oil.	Direct	Direct	Direct	Direct	Direct	Prod. gas
Per cent. of ash.....	2 & 7	8.9	15.0	14.85	5.0	17.0-30
Per cent. fixed carbon.....	68 & 76	51.9	44.5	44.5	55.0	45.0
Oil deg. Bé.....						
Tons charge per ton coal.....	0.77:1	3.05:1	3:1	4:1	2.81:1	2:1
Tons charge per bbl. oil.....						
Labor in 8 hr. shift.....		2 & 2	2 & 2	2 & 2 1/2	2 1/2 & 1 1/2	
Matte, Cu, per cent.....	33.7	53.8	48.3	50	50	50
Matte, sp. gr.....	4.50		4.8			4.77
Slag, SiO <sub>2</sub> , per cent.....	60.5	36.8	42.8	34.5	38.6	41.9
Slag, Fe(Mn)O, per cent.....	28.5	51.9	47.31	43.0	51.4	42.7
Slag, Al <sub>2</sub> O <sub>3</sub> , per cent.....	2.9	8.4	7.5-8.0	8.5	1.5	10.9
Slag, ZnO, per cent.....						
Slag, Ca(Mg)O, per cent.....	20	1.1	1.2			1.1
Slag, Cu, per cent.....	0.5	0.75	0.40	0.60	0.40	0.58
Slag, Ag, oz per ton.....		0.45	0.30	1.0	0.40	
Slags, sp. gr.....	3.21		3.58			3.54



## ATORY FURNACES

			Dust-fired	Oil-fired				
Mont Ore Purchasing Co., 1903	Anacacnda, 1908	Garfield, 1911, coal.	Canadian Copper Co., 1912	Cananea, 1911	Garfield, 1913	Hayden, 1912	Copper Queen, 1913	Steptoe Valley, 1912
37'	112' 4"	112'	112' 0"	100'	112'	112' 3"	92' 7"	120' 10 1/2"
6'	71' 4"	29' 5"	83' 3"	82' 9"	29' 5"	8' 0"	10' 5 1/2"	94' 0 1/2"
8' 0"	35' 0"	47' 5"	83' 3"	17' 3"	47' 5"	73' 3"	50' 5 1/2"	94' 0 1/2"
	16'	35' 2"	28' 9"	19' 3"	35' 2"	37' 11"	31' 8"	26' 10"
14' 6"	19'	19'	19' 0"	19'	19' 0"	16' 0"	17' 3"	18' 11"
5' 0"	7'	7'	7' 9"	8'	7'	7'	8'	18' 11"
22"	1985	1959.5	1970	1688.7	1960	1967	1576	2125
	26"	24"	30"	30"	24"	24"	24"	22" quartz 12" silica brick 7
8'	16'	18'	5	7 (burners)	5	7 (3 in use)	5	7
6'	7'	6' 5"	6"	air 2"	1 1/2"	1 1/2"		1 1/2-1 1/8"
3' 0"	2' 3"	2' 2"		oil 1"				
	2' 0"	1' 10"	10	1000	10	12-14	10	400-600
48.0	112	112.75		13-14				15
	18:1	17.3:1						
2' 0"	5' 4"	3' 9 1/2"	4'	4' 5"	4' 9 1/2"	5'	4' 5 1/2"	7' 4"
4' 10"	7' 6"	6' 2 1/2"	7'	6' 10"	7' 2 1/2"	7' 6"	6' 11 1/2"	9' 4"
2' 4" to 2' 8"	3' 3 1/2"	4' 1"	4'	4' 4"	4' 0"	4' 3"	4' 5 1/2"	3' 11"
	4' 1"	4' 10"	1' 3"	6' 0"	4' 10"	3' 9"	2' 6"	8' 0"
36" X 6"	5' X 3' 2"	7' X 3' - 3"	Throat 7'- 9" X 3' 6"	8' X 5'	7' X 4'	7' 0" X 3' 6"	5' 6" X 3' 10 1/2"	3' 4' 1/2"
30" X 36"	6' X 3' 8"	8' X 12'	2 furnaces	15' X 19'	8' X 12'	6' X 9'	10' X 7'	21 to 60 sq. in.
4' 6" X 4' 6"	Main stack of plant	30' 0"	15' X 19'	11' 6"	30' 0"			15'
80'	do	300	200'	171-1 1/2"	300'			
13	15 every 80 min.	18±	16 slag	10-12	2-4 charges of 5-6 tons	300'	300'	300'
5 1/2	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous	Continuous
70	300	250-390	525	225	340	340-400	285	371
	0.150	0.103	0.27	0.123	0.173	0.17-0.24	0.181	0.196
5:1 Direct	13.4:1 Direct	3.5:1 Direct	Dust	4.4:1 Oil	3.0-3.5:1 Oil	3-4:1 Oil	3.5:1 Oil	4:1 Oil
7-10	11	6	10					
50-52	56	48		15	12.5-14.0		15.75	14-16
2.5:1	48:1	3.5-4.75:1	10.5	1.121	0.80	0.7-0.9	1.098	0.85
2 1/2 & 1 1/2		4 & 2		4 & 3	2 & 2 1/2	3	8.5	9*
55	46	33-48	33 Cu Ni	35	45	45-48	37-27	35-45
49.0	37.8	4.85-4.56		4.85	45		4.60	5.0-5.6
32-36	38.6	43.4	31.10	36.8	29	44	35.5	41.9
	6.0	33.5	57.85	35.1	6	29-30	33.4	33.6
		5.8	4.15	10.5		6-8	11.15	10.6
				3.0	1		1.0	
	40-45	12.8	1.50	9.3	17	6	1.8	7.4
0.65	0.37	0.41	Cu 0.24 Ni 0.50 S 1.27	0.36	0.4	0.40-0.52	0.51	0.45
		0.1		0.11				
		3.40			3.35	3.3	3.52	3.21

\* Originally 6' 10".

\* Originally 6' 10" X 3' 0".

\* Including delivery, one foreman for plant.

TABLE 52.—REVERBERATORY FURNACE  
Construction and Operation

	Anaconda (Montana)	Cananea (Mexico)	Great Falls (Montana)	Garfield (Utah)	Steptoe (McGill) (Nevada)		Tooele (Utah)
					(Coal) fired	(Oil) fired	
Number of furnaces.....	8	2	3	6	5		5
Average tonnage per day.....	259— 15 tons	102.3 7½ to 9 tons	203— 35 tons	240— 6 to 24 tons	230— 14 tons (var.)	322— 14 tons (var.)	225— 13 tons
Average weight of charge per ton fuel.....	25	5.86	100	3.50 to 4.00	3.24	3.80	3.00
Average temperature of charge entering furnace.....	510° C. (Est.)	260°–288° C.	420° C.	204°–371° C.	260° C.	260° C.	399° C.
Kind of fuel used.....	Run of mine coal	California crude oil	Producer gas	Bituminous coal		California crude oil	Run of mine coal
Character of charge:							
Calaine (hot).....	84.95 %	50.0 %	66.00 %	75 % to 78 %	61.3 %	56.8 %	95.00 %
Calaine (cold).....	15.05	50.00	34.00	19 % to 16 %	1.2	1.4	5.00
Flue-dust.....				6.00	9.8	7.4	
Conv. slag.....					12.5	13.2	
Secondaries (cold).....					15.2	19.5	
Flux and fettling ores (cold and wet).....							
Dimensions of hearth.....	111' 8" X 19' 0"	100' X 19'	41' 6" X 15' 9"	112' X 19'	120' 10" X 19'		102' X 10'
Dimensions of fire-box.....	7' X 16'	None	Gas fired	7' X 18'	None		7' X 16'
Top of grate bars to top of bridge.....	24"	None	Gas fired	33"	33½"		40"
Top of grate bars to under side of roof.....	70"	None	Gas fired	45" to 48"	85½"		78"
Height of "verb" or vulcatory above skim plate.....	36"	36½"	Gas fired	36" to 38"	36		36"
Dimensions at throat of furnace.....	7' X 4' 11"	7' X 1' 9"	Gas fired	7' X 3' 3"	6' 10" X 3'		7' X 4' 1"
Dimensions of flue beyond throat (damper flue).....	36" by 54" (natural draft)	7' X 6'		39" X 64"	(Not given)		36" X 60"
Draft in inches of water at bridge.....	0.75"–1"	No data	0.2"	0.6"	0.2"–0.5"		0.8"
Draft in inches of water at throat.....	1.3"–1.7"	0.13"	0.3"	0.8"	0.7"–1.2"	0.9"	0.6"
Draft in inches of water—main flue beyond boilers.....	1.5"–2"	0.9"	1.5"	1.65"	1.25"		1.75"
Dimensions of main flue.....	15' X 20'	115 sq. ft.	20' X 48'	19' 8" X 22' 6"	20' 3" X 8' 6"		18' X 20'
Dimensions of chimney.....	300' X 30'	187' X 12' 6"	506' X 50'	300' X 30'	300' X 15'		350' X 25'
Height of top of stack above grate.....	740'	198'	768'	504'	316' 9½"		412'
Temperature of gas at bridge.....	1538° C.	1482°–1538° C	1455° C.	1422°–1538° C.	1482°–1640° C.		1422° C.
Temperature of gas at throat.....	1205° C.	1260°–1316° C	1397° C.	1094° C.	1205° C.		1093° C.
Temperature of gas at far side of boilers.....	360° C.	260° C.	(No boilers)	483° C.	427° C.		412° C.
Average boiler h.p. per furnace from waste heat.....	560 h.p.	971 h.p. <sup>1</sup>	None	380 h.p.	486 h.p.	632 h.p.	390 h.p.
Per cent. fuel recovered as steam.....	32.81	56.62	None	27.00	32.3	33.8	41.2
Per cent. fuel recovered from ashes.....	7.50	None	5.00	9.50	5.05		None
Ratio of concentration.....	4.79	4.96	4.30	3.50	3.31	3.40	9.00
Tons charge per million B.t.u.....	0.182	0.1574	0.115	0.147–0.167	0.122	0.171	0.165

<sup>1</sup> Economizers are installed at this plant beyond boilers.

TABLE 52.—REVERBERATORY FURNACE.—Continued  
Materials Used and Produced

	Copper, per cent.	Silver, oz. (per ton)	Gold, oz. (per ton)	Per cent. SiO <sub>2</sub>	Per cent. Fe & Mn	Per cent. CaO	Per cent. S	Per cent. Al <sub>2</sub> O <sub>3</sub>
Charge	Anaconda.....	9.31		0.028	28.63	3.59	7.34	5.22
	Cananea.....	6.43	6.43	0.14	26.96	2.58	0.59	5.54
	Great Falls.....	2.22	3.77	0.0236	31.34	4.20	11.40	6.40
	Garfield.....	9.47	3.50	0.16	26.91	11.50	10.50	4.50
	Step toe, coal-fired, oil-fired.....	12.00	0.401	0.078	30.00	5.80	0.50	5.30
	Tooele.....	13.60	0.345	0.078	25.90	5.40	6.50	6.90
Slag	Anaconda.....	2.90	3.80	0.11	37.50	3.80		
	Cananea.....	0.39	0.19	0.0006	32.83	4.62	0.91	7.03
	Great Falls.....	0.35	0.11	.....	33.58	3.83	1.08	7.96
	Garfield.....	0.35	0.12	trace	23.64	11.60	0.48	9.40
	Step toe, coal-fired, oil-fired.....	0.45 <sup>1</sup>	0.08	trace	20.58	17.50	1.00 app'x	5.50
	Tooele.....	0.50 <sup>1</sup>	0.06	0.005	28.90	10.50	0.40	7.60
Matte	Anaconda.....	0.43	0.02	0.007	25.90	10.90	0.20	8.00
	Cananea.....	41.68	0.45	0.008	36.93	4.00		
	Great Falls.....	31.91	28.40	0.130 (Insl)	26.54		25.76	
	Garfield.....	31.96	11.34	0.07	37.17		26.87	
	Step toe, coal-fired, oil-fired.....	42.00	12.00	0.085	35.54		26.70	
	Tooele.....	41.76	10.00	0.50	27.00		26.00	
Fuel	Anaconda.....	42.09	1.25	0.25	29.00		25.10	
	Cananea.....	23.00	0.22	0.91	29.10		24.80	
	Great Falls.....		27.50	0.85	43.00		26.50	
	Garfield.....							
	Step toe, coal-fired, oil-fired.....							
	Tooele.....							
Gas—Great Falls.	Anaconda.....	6.13	36.28	45.42	12.17	12,390—	11,710—	
	Cananea.....					No data	18,600—	
	Great Falls.....	7.70	23.70	46.00	28.60	No data	9,382—	
	Garfield.....	8.00	39.40	46.40	6.20	No data	12,000—	
	Step toe, coal-fired, oil-fired.....	2.00	39.10	51.50	7.40	13,000—		
	Tooele.....	6.00	38.00	45.00	11.00	18,220—	11,500—	
Per cent. moisture								
Per cent. V. C. M.								
Per cent. ash								
Per cent. fixed carbon								
Per cent. CO <sub>2</sub>								
Per cent. CO								
Per cent. CH <sub>4</sub>								
Per cent. H								
Per cent. N								

<sup>1</sup> Converter slag is poured into reverberatories at these plants, thus raising copper assay, as only 75 per cent. of copper in converter slag is recovered.

### 138. References to Some Reverberatory Furnace Smelteries.<sup>1</sup>

**139. The Working Bottom.**—This must be refractory to resist high temperatures, strong to hold the heavy bath of matte or copper, dense to prevent percolation of matte or copper, and elastic to stand changes in temperature without cracking. The bottom used to be made universally of silica more or less pure fritted in place to form a single block. Sand-bottoms have been replaced in some instances by bottoms of silica-brick. At first they did not prove altogether satisfactory, as it was difficult to make the joints sufficiently tight to prevent matte from percolating and floating the brick, but this has been overcome. Clay bricks have been frequently advocated<sup>2</sup> and are said to be used in Wales and New South Wales. A basic bottom has been recommended by Gilchrist<sup>3</sup> for the treatment of white metal, impure bottoms and blister

<sup>1</sup> AMERICAN SMELTERS SECURITIES CO.: Mathewson, *Tr. A. I. M. E.*, 1912, XLIV, 781.

ANACONDA: Mathewson, *Eng. Min. J.*, 1903, LXXVI, 165; *Min. Ind.*, 1902, XI, 200; *Tr. A. I. M. E.*, 1912, XLIV, 781; Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 258; Austin, *op. cit.*, 1906, XXXVII, 431; Corresp. *Mines and Minerals*, 1907, XXVIII, 131, 248; Offerhaus, *Eng. Min. J.* 1908, LXXXV, 1189, 1234.

BALAKLALA SMELTERY: Report, *Eng. Min. J.*, 1909, LXXXVII, 501; Martin, *Min. Sc.*, 1911, LXIII, 338.

CANAJEEN SMELTERY: Brinsmade, *Mines and Minerals*, 1907, XXVII, 465; Ricketts, *Tr. Inst. Min. Met.*, 1909-10, XIX, 147; *Min. World*, 1909, XXXI, 1115; *Eng. Min. J.*, 1910, LXXXIX, 314; Mathewson, *Tr. A. I. M. E.*, 1912, XLIV, 781.

GARFIELD SMELTER: Beason, *Eng. Min. J.*, 1906, LXXXI, 509; Ingalls, *op. cit.*, 1907 LXXXIV, 575; Brinsmade, *Mines and Minerals*, 1908, XXVIII, 305; Mathewson, *Tr. A. I. M. E.* 1912, XLIV, 781.

GREAT FALLS: Hofman, *Tr. A. I. M. E.*, 1909, XXXIV, 289; Mathewson, *op. cit.*, 1912, XLIV, 781.

INTERNATIONAL (TOOELE) SMELTER: Editor, *Mines and Methods*, 1909, I, 149; Palmer, *Min. World*, 1910, XXXIII, 945; Editor, *Eng. Min. J.*, 1910, XC, 1059; Redpath-McGregor, *Mines and Minerals*, 1911, XXXI, 322; Corresp. *Min. Sc. Press*, 1912, CIV, 371; Mathewson, *Tr. A. I. M. E.*, 1912, XLIV, 781; Thomson-Sicka, *op. cit.*, 1913.

KEDABEG (Kankasus): Kölle, *Eng. Min. J.*, 1905, LXXX, 201; *Min. Mag.*, 1905, XII, 471; *Tr. Inst. Min. and Met.*, 1904-05, XIV, 497; Schnabel, *Eng. Min. J.*, 1891, LI, 566; Golowatscheff-Lange, *Glück Auf*, 1913, XLIX, 424, 526, 732; *Eng. Min. J.*, 1913, XCV, 15 (Hahn).

KYSHTIM SMELTERY: Carlyle, *Eng. Min. J.*, 1912, XCIII, 1231; Mathewson, *Tr. A. I. M. E.*, 1912, XLIV, 781; Asejew-Lange, *Metall-Erz.*, 1913, X, 108.

STEPTOE VALLEY: Ingalls, *Eng. Min. J.*, 1907, LXXXIV, 815; Editor, *Mines and Methods* 1909, I, 72; Humphreys, *Min. World*, 1909, XXX, 273; Palmer, *op. cit.*, 1910, XXXII, 691; Mathewson, *Tr. A. I. M. E.*, 1912, XLIV, 781.

UNITED VERDE COPPER CO.: Vail, *Eng. Min. J.*, 1913, XCVI, 287, 341.

WALLAROO AND MOONTA: Cloud, *Tr. Inst. Min. Met.*, 1906-07, XVI, 55; *Eng. Min. J.*, 1907, LXXXIII, 324; Williams, *Eng. Min. J.*, 1908, LXXXVIII, 55.

YAMPA SMELTERY: Christensen, *Min. World*, 1909, XXX, 621; Palmer, *Min. Sc. Press*, 1909, XCIX, 225; *Mines and Minerals*, 1910, XXXI, 14.

<sup>2</sup> Peters, *Min. Ind.*, 1893, II, 270; "Modern Copper Smelting," 1895, p. 466.

Hall, *Eng. Min. J.*, 1895, LIX, 363.

Terrill, *op. cit.*, 1898, LXVI, 665.

Hering, *Berg. Hüttenm. Z.*, 1895, LIV, 294.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1891, X, 4; *School Min. Quart.*, 1891-92, XIII, 87; *Berg. Hüttenm. Z.*, 1891, I, 97; *Eng. Min. J.*, 1890, XLIX, 566; 1891, LI, 141; *Coll. Guard.* 1891, LXI, 69.

Styri, *Metallurgie*, 1912, IX, 426, 449.

copper in order to facilitate the removal of As and Sb, and to reduce the amount of slag that is formed. The basic hearth, while it stood satisfactorily, was not especially successful in removing impurities; at first it readily absorbed As and Sb, but ceased to do this later on and even gave up some impurity to subsequent charges. It may be recalled that in the Knudsen process (§ 109) and in the basic matte converter (§ 171) magnesite brick form a dense and resisting lining as long as the temperature does not exceed  $1150^{\circ}\text{C}$ . The reverberatory furnaces of the Canadian Copper Co. have magnesite bottoms and sides and are working satisfactorily. Chromite and chrome brick have been tried as a refractory to form a bottom; though they were not melted or fluxed, they crumbled away.<sup>1</sup> Chrome brick are used at the slag line in matting and in acid refining furnaces, and give satisfaction. Recently Addicks and Browne,<sup>2</sup> constructed a refining furnace having a working bottom of magnesite, and sides and roof of chrome brick.

Silica sintered in places still retains its place as the common material for the working bottom. This is 24–30 in. thick and slopes from the ends and the back toward the deepest point, the tap-hole at the front. The depth of the basin, *i.e.*, the distance from the tap-hole to the level of the skim-plate is 13 or 14 in. Table 53 gives analyses of the sands used by some smelting plants. There are two varieties<sup>3</sup> of crystallized  $\text{SiO}_2$ , quartz with specific gravity 2.65 and tridymite with specific gravity 2.32. Upon heating, quartz changes slowly into tridymite with an increase in volume of 20.7 per cent.<sup>4</sup> The more tridymite prevails in the original sand, or rock, usually crushed to pass a 10-mesh sieve, or the more the original quartz has been converted into tridymite by calcining, the more desirable will be the sand. Further, the more finely divided the particles of  $\text{SiO}_2$  and the associated  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ , etc., the more easy will be the conversion of quartz into tridymite, and the stronger will be the hearth on account of the even distribution of the glassy bond which holds together the particles of  $\text{SiO}_2$ . Lastly, the sand may contain enough bases to be slightly fus-

TABLE 53.—SILICA SAND FOR WORKING BOTTOM

Locality	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{CO}_2$ $\text{H}_2\text{O}$	Total	Reference
Wales.....	86.0	1.6	1.2	5.7	0.8	4.5	99.8	Le Play, <i>op. cit.</i> , 71.
Wales.....	87.87	2.13	2.72	3.79	0.21	2.60	99.32	Percy, <i>Metallurgy</i> , 1861, p. 238.
Anaconda....	97.5	1.17	0.11	0.20	.....	.....	98.98	Austin, <i>Tr. A. I. M. E.</i> , 1906, XXXVII, 431.
Boston and Montana.	95.0	.....	.....	.....	.....	.....	.....	Hofman, <i>op. cit.</i> , 1904, XXXIV, 258.
Garfield.....	92.0	2.0	1.4	1.8	.....	.....	.....	Moore, <i>Eng. Min. J.</i> , 1910, LXXXIX, 1023.
Cananea.....	95.0	.....	.....	.....	.....	.....	.....	Ricketts, <i>Tr. Inst. Min. Met.</i> , 1909–10, XIX, 147.

<sup>1</sup> Moore, *Eng. Min. J.*, 1910, LXXXIX, 1023.<sup>2</sup> *Eng. Min. J.*, 1914, xcvi, 421, U. S. Patent No. 1083719, Jan. 6, 1914.<sup>3</sup> Hofman, "General Metallurgy," 1913, p. 365.<sup>4</sup> Grum-Grzimallo, *Stahl u. Eisen*, 1911, xxxi, 224.

ible, as indicated by the material used in Wales; or it may be practically infusible, when either a small amount of crushed slag will be mixed in to serve as a bond, or the sand will be fritted in the furnace and some slag melted down upon the hearth to fill in the interstices and bind together the particles.

As to the manner of putting in a sand-bottom four methods may be distinguished: The sand mixture is moistened and rammed; it is put in in thin layers which are severally sintered, in two layers, or in a single layer to be sintered. The practice of ramming and of putting in in thin layers is not found in the United States; two layers are sometimes found in furnaces in which matte is concentrated or metallic copper produced. A single layer is common with ore-furnaces.

(1) With ramming,<sup>1</sup> the sand, or sand mixed with as much as 10 per cent. slag is moistened as brasque would be, and rammed down firmly, giving the hearth with its tap-hole the desired form. The furnace then is warmed very gradually to drive out all moisture; when dry, the temperature is slowly raised to the highest possible degree and held there until the bottom has sintered to some depth, when it is "seasoned," *i.e.*, soaked with slag or slag and some matte.

At the works of the Electrolytic Refining & Smelting Co. of Australia<sup>2</sup> the working-bottom of a furnace, with hearth 34×17 ft., consists of a rammed mixture of chromic iron ore and fire-clay. The foundation of the furnace is a bed of concrete 2 ft. 6 in. thick; the foundation for the working-bottom consists of a 12-in. bed of concrete followed by a course of red brick laid flat, a layer of rammed brasque (fire-clay+coke+sand) 6 in. thick at the center and increasing toward the sides, a course of 9 in. of local fire-brick, and one of 9 in. of Scotch fire-brick. On this foundation is tamped with hot irons in  $\frac{1}{2}$ -in. layers ( $\frac{1}{8}$  in. thick when rammed) a moistened mixture of 3 vol. chromic iron ore ( $\frac{1}{8}$  in.) and 1 vol. fire-clay as a working-bottom, 6 in. thick at the center and 15 in. at the sides. The brick side walls are stepped out  $1\frac{1}{2}$  in. for three courses and then stepped in  $1\frac{1}{2}$  in. for the next three courses to form a recess for holding down the bottom. The bottom requires 17 tons of chromic iron ore, 3.5 tons of fire-clay, and thirteen 8-hr. shifts of 7 men. The bottom resists corrosion and is non-absorbent.

(2) In the second method the sand or sand-slag mixture is spread in thin layers to be sintered severally until the bottom has attained the desired thickness. Sand mixture is then introduced with a paddle, molded and patted with a bowl-shaped long-handle tool to give the hearth the form of a basin, heated until the surface sinters, and then patched with new material if found necessary. After this, the last heat is given to season the bottom.

(3) Putting in the bottom in two layers<sup>3</sup> represents a more modern method. Let a small hearth, 16 by 12 ft., such as is frequently used in the concentration

<sup>1</sup> Hering, *Berg. Hüttenm. Z.*, 1895, LIV, 295.

<sup>2</sup> Schroeder-Longworth, *Met. Chem. Eng.*, 1911, IX, 220.

<sup>3</sup> Levy, *Rev. Univ. Min.*, 1884, XVI, 286-339; *Berg. Hüttenm. Z.*, 1885, XLIV, 396, 439, 469, 485, 497, 507.

Peters, "Modern Copper Smelting," 1895, p. 483-487.

of matte, serve as example. A layer of clay from 2 to 4 in. thick is spread over the bottom in order to prevent any percolating matte from reaching the brick-work; a fire is kindled on the clay bed and in the ashpit to dry and warm the furnace and the bed, the temperature is raised gradually to bring the hearth and roof to a dark red which takes about four days. By this time all moisture and organic matter have been expelled. The wrought-iron grate bars are put in place, a fire is started and urged for 12 hr., when the interior will be at a light red. From 6 to 10 tons of sand are charged, the amount required to form a bottom from 12 to 15 in. thick. The sand is thoroughly calcined to remove  $H_2O$ ,  $CO_2$ , and organic matter, and, as recently shown, to change quartz in part into tridymite; this takes from 5 to 8 hr., the sand being rabbled more or less to bring all particles to the surface. The sand suitably prepared is given the shape of a basin sloping from the ends and the back to the deepest point at the front, the tap-hole, with rabble and paddle, and patted and beaten with a bowl-shaped long-handle tool. The formed hearth is ready to be sintered. The tap-hole is bricked up, the doors are closed, luted, and covered with loam; the fire is urged to bring the hearth to a white heat, which takes about 8 hr., and held there for 6 hr. more, the progress being watched through a peep-hole in the rabbling-door closed by a clay plug. The sand-bottom will have sintered to a depth of about  $\frac{1}{2}$  in., the side walls and roof will have become glazed. Firing is stopped, and the furnace allowed to cool down slowly to a dull cherry-red without admission of air. From 1.5 to 2.0 tons of acid slag of chestnut size is spread evenly over the hearth with a paddle, melted down in about 2 hr., and the excess not absorbed by the bottom removed with a rabble.

Peters<sup>1</sup> recommends melting down a second charge of slag to which some 30-per cent. copper matte has been added, in order to soak the lower sand-bottom with low-grade matte and thus prevent matte of higher grade from filling the open spaces between the grains of sand.<sup>2</sup>

Whether a single slag-charge be given, or two, it is essential that the lower sand-bottom now finished be allowed to cool to a dark red and to harden. This prevents the upper bottom, which has to be replaced occasionally, from adhering to the lower. The sand for the upper bottom, which is from 12 to 18 in. thick, is introduced and treated in the same manner as was the lower. The sand has been sintered at the surface, and this is strengthened by cementing with slag; the bottom has been soaked (seasoned) with slag or with slag and matte. If soaking with matte has been omitted, a large part of the matte produced in the first ore-charge will disappear in the bottom. Matte-concentrating reverberatory furnaces are seasoned with matte of lower grade than the one that is to be produced; thus white-metal furnaces are worked for two or three days as ore-furnaces; blister-furnaces as white-metal furnaces. As the absorbed matte affects the metal or matte to be produced, a high-grade charge may not be worked on a bottom that has been seasoned with matte charged with impurities.

When the upper sand-bottom is finished and has cooled to a dark red, slag

<sup>1</sup> *Op. cit.*, p. 486.

<sup>2</sup> Hall, "Soaked Bottoms," *Eng. Min. J.*, 1903; LXXVI, 342.

is spread over the junction of bottom and side wall to cement the two. Last comes the fettling, a moistened mixture of crushed quartzite and clay, introduced through the side-doors to fill and round off the rectangular space between vertical side- and end-walls and the horizontal sand-bottom; the fettling is packed down with the flattened and bent end of a heavy iron rod. The fire is urged again to dry the fettling. The furnace is now ready, receives small charges at first, and is tapped dry for several consecutive charges before any matte is allowed to accumulate.

(4) Putting in the bottom in a single layer is well illustrated by the practice of R. L. Lloyd with the gas-fired regenerative furnaces, hearths 42 ft. 6 in. by 15 ft. 9 in. (Table 51), at Great Falls, Mont. It is presupposed that the furnace is new and requires drying and warming. A light wood fire is started on the hearth in half a dozen places, and the valves reversed every half hour. Firing is continued for about ten days, when the furnace will be at a dull red; in two days more it will be hot enough to ignite producer gas. The gas is turned on, in small amounts at first; on the fourth or fifth day (the sixteenth or seventeenth after starting) the furnace will be at a bright cherry red.

Five tons of sand are charged through the hoppers in the roof and spread, covering the hearth to a thickness of 2 in. The sand is calcined, turned over, and the furnace brought to a normal heat; charging of sand and heating it are continued in 5- or 6-hr. intervals until about 60 tons have been introduced, care being taken to have the sand thoroughly calcined. The furnace is now brought, in from 36 to 48 hr., to the highest heat obtainable without endangering the brickwork, and the sand brought to a set which amounts to about 3 in. in thickness. The high heat is maintained for 16 hr., and the furnace then cooled down in 8 hr. to a dull cherry red. Enough calcines (giving a 45-per cent. copper matte) are dropped through the roof to cover the hearth to a depth of 3 in.; they are melted down and absorbed by the sand-bottom. The furnace is cooled as before, and a second charge of calcines given and melted. Part only of the charge will be taken up by the hearth; the rest is tapped out.

The furnace is again cooled; from 12 to 15 tons of ore-charge are given, melted down, and the furnace tapped dry and cooled to a dark red, but more slowly than before. It is again fired up, worked for three days as under normal conditions, and then tapped dry and allowed to cool to a cherry red. It is now safe for any kind of work. The time required to bring a new, cold furnace to this point is three weeks. The object of the repeated coolings is to harden the bottom.

A bottom put down without cooling is likely to be mushy when hot, even though it be hard when relatively cool.

A manner in which the putting of a sand-bottom may be hastened is shown by following the former practice of the Butte & Boston works, Butte, Mont. The furnace (see Table 51) had a hearth 20×50 ft. and required 73 tons of crushed quartzite for the working bottom. The furnace, dry and warm, was charged with from 6 to 7 tons of sand; heated for 6 hr.; and rabbled at intervals. Charging and rabbling were continued, with the fire being kept up, until about one-half of the sand required had been introduced, when the temperature was brought



to a white heat and the surface of the sand fritted. After cooling down the furnace, the other half of the sand was charged and treated in the same manner as the first. Converter-slag was poured in to cement together the sand particles and to soak into the bottom, and the excess slag withdrawn. From three to four charges of calcines were worked, and the matte tapped only after the last charge had been finished. The time required to put in the bottom was four days.

In building a bottom of silica-brick, there is first rammed in firmly a sand-bottom to the form of an inverted arch; on this are laid the silica brick having a length of 12-15 in. In order to provide room for expansion, which amounts to  $\frac{5}{16}$  in. to the running foot, cardboard is placed between bricks every few feet; at the firing end, where the heat is greatest, silica-brick and card board are used alternately.

The manner in which the magnesite bottom was put in at Copper Cliff has been given on page 244.

In starting the 100-by 19-ft. direct-fired Anaconda furnace,<sup>1</sup> which is presupposed to be dry, a wood fire is made as usual and this replaced by coal when the furnace has become warm. In heating, care is taken to loosen the nuts of the tie rods to allow for expansion after the roof (always of silica-brick, 15-18 in. long) has been allowed to rise for 2 in. After two days' warming and heating, the first charge is dropped. Table 54 gives the record of starting. The

TABLE 54.—RECORD OF STARTING UP AN ANACONDA FURNACE, 100 BY 19 FT.

Date	Coal, tons	Charge smelted, tons	Charge, smelted, tons per ton coal
July 23.....	14.4	.....	.....
July 24.....	39.6	35.3	0.89
July 25.....	52.4	54.1	1.03
July 26.....	50.1	76.7	1.53
July 27.....	53.1	120.0	2.26
July 28.....	52.2	104.8	2.00
July 29.....	56.4	118.4	2.10
July 30.....	52.2	125.5	2.41
July 31.....	55.3	237.1	4.29
Aug. 1.....	53.4	245.5	4.60
Aug. 2.....	56.3	245.6	4.36

furnace is not tapped before it contains a charge of 250 tons of matte. It is evident that it takes from 10 to 15 days to get the furnace into regular working order. The furnace is clayed once a month; it is shut down once in eight months to undergo full repairs.

**140. Fuels.**<sup>2</sup> —The fuels used in firing copper reverberatory smelting furnaces are bituminous coal, producer gas from bituminous coal, fuel-dust, wood, producer gas from wood, and oil. Bituminous coal in the common fuel; in recent years oil has replaced coal in many of the western smelteries of the United States.

<sup>1</sup> Offerhaus, *Eng. Min. J.*, 1908, LXXXV, 1237.

<sup>2</sup> Gabrill, *Eng. Min. J.*, 1910, LXXXIX, 826.

**141. Bituminous Coal<sup>1</sup> and Producer Gas.**—Most furnaces are direct fired; in a few cases, as, *e.g.*, at Great Falls, the coal is gasified in a producer,<sup>2</sup> and the smelting furnace provided with regenerators. The second arrangement had

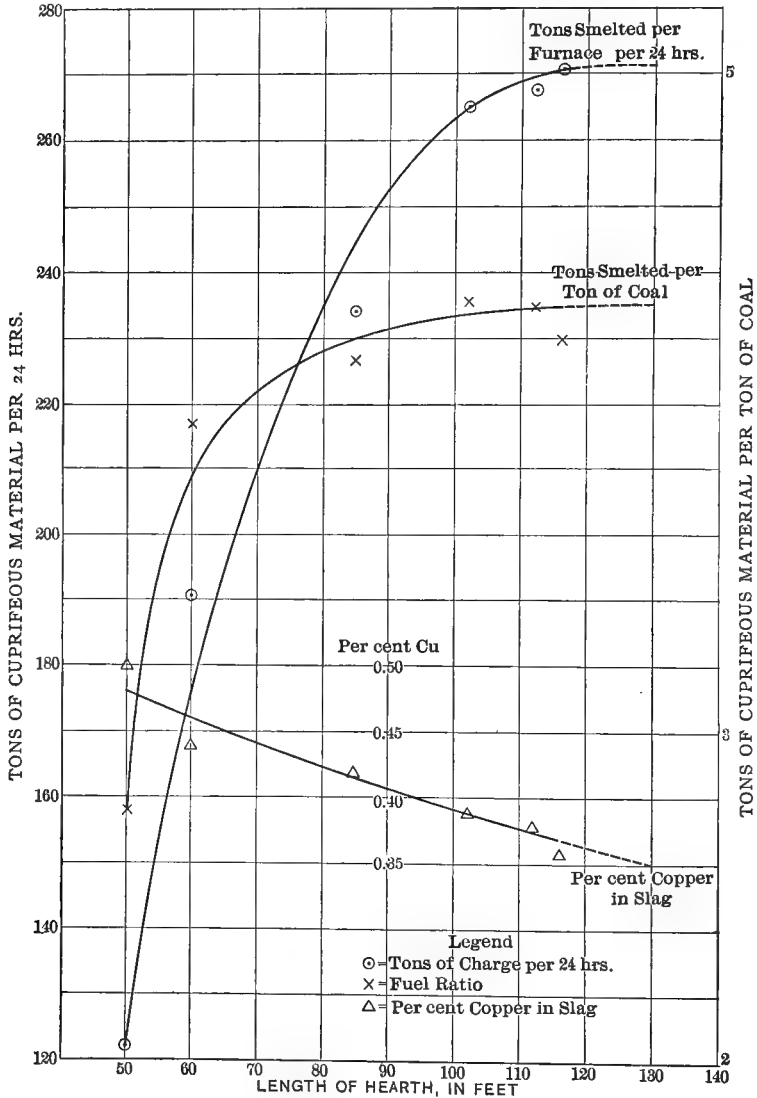


FIG. 306.—Relation of tonnage, fuel consumption and copper-content of slag at Anaconda.

many advantages in comparison with the first in spite of the expense of the regenerators and their frequent repair necessitated by the choking and slagging effect

<sup>1</sup> Demond, Bull. A. I. M. E., August, 1914, "Economy and Efficiency in Reverberatory Smelting."

<sup>2</sup> Historical Note: Simpson, Min. Mag., 1913, VIII, 211; Met. Chem. Eng., 1913, XI, 291.

of the ore dust, until waste-heat boilers were attached to direct-fired furnaces. These have proved so efficient in recovering as steam 30-50 per cent. of the fuel consumed that regenerative ore-smelting furnaces will be built henceforth only under special conditions.

Gas-firing with producer attached to reverberatory furnace provided with waste-heat boilers, the producer to be fed as well as cleaned (grated) mechanically, is contemplated for the new smelter at Great Falls.

With direct firing the question of natural and forced draft has to be considered.<sup>1</sup> The draft at the fire-bridge is about 0.5 in. water and at the flue-bridge 1 in. (Table 52). Most copper metallurgists prefer natural draft, mainly on account of the fact that the cleaning of the grate (grating) is made relatively easy, and little time thus lost in the smelting. With forced draft, the heat in the fire-place becomes locally so intense as to form large hard clinkers which adhere to the grates and walls. The breaking takes much time and labor, and causes the furnace to remain idle during the grating. In order to prevent the latter, the fire-box has been divided into two or three compartments by partition walls; this permits grating one compartment while the others are being fired. With natural draft, chilling false air is likely to be drawn into the furnace, which is not the case with forced draft.

In burning bituminous coal the limit of economic length of hearth is reached much earlier than with liquid or gaseous fuel. In Fig. 306 Mathewson records the experience at Anaconda. It shows that the tonnage of cuprifous material smelted in 24 hr. grows uniformly with increase of length of hearth to about 90 ft.; that the rate of advance is more slow to about 115 ft., and then practically ceases. The Cu-content of the slag decreases with the length of the hearth as long as the temperature at the flue-bridge is sufficiently high to keep the slag fluid. The coal consumption decreases very fast until the length of the hearth is about 80 ft., between 80 and 100 ft. it is more slow, and ceases at about 110 ft. Coal-fired furnaces will therefore not be made longer than 100 ft.

**142. Fuel-dust.**<sup>2</sup>—Work with this method of firing was not entirely satisfactory until Browne overcame the earlier difficulties at Copper Cliff, Ont. One is justified in expecting that with continuous firing, on account of the absence of stops of from 0.5 to 2 hr. for grating, the heat generated will be uniform and the flame steady, and that with a complete rapid combustion, not requiring a great excess of air, the temperature will be high. Unexpected mechanical difficulties, which had a harmful effect, had to be overcome before success could be attained. Some of these difficulties were: that carbon settled upon the charge forming an insulating blanket which caused the slag to become sticky, and that only part of the ashes was slagged, the rest settling in the flues. Sörensen<sup>3</sup>

<sup>1</sup> See Demond, *loc. cit.*

<sup>2</sup> Hofman, "General Metallurgy," 1913, pp. 183-189, *Eng. Min. J.*, 1906, LXXXI, 274 (Sörensen); 1908, LXXXV, 121 (Editor), 326 (Trent), 582 (Shelby), 269, 660 (Thomas), 778 (W. B. S.) 915 (B. S. F.), 1017 (Richmond), 1064 (Robinson); *J. Canad. Min. Inst.*, 1912, xv, 115 (Browne).

<sup>3</sup> *Loc. cit.*

found at the works of the Utah Consolidated Copper Co., that, notwithstanding these drawbacks, he was able to smelt 30 per cent. more ore with 16–20 per cent. less fuel than in another furnace of the same plant which was fired direct.

Vertical longitudinal and horizontal sections through the firing-end of one of the two reverberatory furnaces of the Canadian Copper Co., Copper Cliff, Ont., were given in Figs. 275 and 276. The coal, which contains 10 per cent. ash, is crushed to  $\frac{1}{2}$  in. in two coal crackers at the rate of 50 tons in 10 hr., freed from water in Ruggles-Coles dryers, ground in two Raymond impact pulverizers and sucked into separators whence the dust, nearly all 200-mesh, is delivered by means of screw-conveyors to V-shaped dust pockets at the end of the furnaces, Fig. 275, each with five discharges, 2 ft. 6 in. by 1 ft., Fig. 276. From these the dust is fed by variable speed 4-in. screw-conveyors (drop-hangers shown in Fig. 275) into five 12-in. pipes, which receive their air through a 14-in. pipe from a No. 8 Monogram (B. F. Sturtevant) blower, and end in 5-in. nozzles extending into the furnace. A feeder makes 24 r.p.m. and feeds 0.65 lb. dust per revolution. A furnace burns 50 tons of dust in 24 hr.; the flame is 100 ft. long.

**143. Wood and Producer Gas.**—Wood will be used only when other fuels are not available, as its calorific power is low and as its volume is large. Though Gabrill<sup>1</sup> calculates that air-dried wood (20 per cent.  $H_2O$ ) cannot furnish the heat required in a copper reverberatory furnace, it may be recalled that Lebedeff-Pomeranzeff<sup>2</sup> are using it just for this purpose in their furnace, which has regenerators for preheating the air. Further, Canfield<sup>3</sup> reports smelting per day 15 tons of roasted concentrates and siliceous ore with 7.7 cords of wood in a furnace, 16 by 9 ft., having a grate area of 16.5 sq. ft. and a depth from bridge to grate of 3 ft.; he used forced draft and made a slag with  $SiO_2$  40 per cent.<sup>4</sup> Usually, however, if wood is to be used, it will be gasified in a producer, and the water-vapor condensed before the gas enters the regenerator. An early example of a Swedish furnace used for refining copper is given by Peters.<sup>5</sup>

One of more recent date is that of Kyshtim, Russia,<sup>6</sup> where, in a regenerative furnace with hearth 35 by 15 ft., from 82 to 98 tons of charge assaying 3.1 per cent. Cu are smelted in 24 hr. making matte with Cu 11.35–5.70, S 26.5–23.1, Fe 53.37–58.83,  $SiO_2$  0.80–1.50,  $Al_2O_3$  2.38–(?), CaO 0.25–0.31 per cent.; and slag with  $SiO_2$  39.61–38.68, FeO 39.06–27.70, CaO 3.58–6.53,  $Al_2O_3$  10.98–10.42,  $BaSO_4$  8.24–7.97, Cu 0.09–0.08, S 2.34–2.11 per cent. The surface of the checkers is 9354 sq. ft. and the useful area, 7405 sq. ft.; the sectional area of the checkers 527 sq. ft.; the surface of the gas checkers 7513 sq. ft. and the useful area 60.7 sq. ft.; the sectional area of the gas checkers 495 sq. ft. The average analysis of producer gas is  $CO_2$  7.47, CO 26.22, H 8.3,  $CH_4$  5.86,  $C_2H_4$

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Metallurgie*, 1910, VII, 332.

<sup>3</sup> *Eng. Min. J.*, 1902, LXXIII, 525.

<sup>4</sup> See also, Hall, *op. cit.*, 1903, LXXVI, 342; 1911, XCII, 1024.

<sup>5</sup> "Modern Copper Smelting," 1895, p. 515.

<sup>6</sup> Carlyle, *Eng. Min. J.*, 1912, XCIII, 1231.

Mathewson, *Tr. A. I. M. E.*, 1912, XLIV, 781.

Asejew-Lange, *Metall-Erz.*, 1913, X, 108.

0.79 per cent. vol., that of the products of combustion in the stack  $\text{CO}_2$  12.2, O 6.3, N 71.5 per cent. vol.

The pressure of the gas at the reversing valve is 0.11 in. water, the suction at the stack 0.98 in. The temperature of the gas entering the regenerator is  $68^\circ\text{C}$ . (?) and leaving the stack  $385^\circ\text{C}$ . The average temperature of the furnace is  $1600^\circ\text{C}$ ., that of the gases entering the checkers  $1300^\circ\text{C}$ . The consumption of wood is 3.13 cords per ton of charge.

In fact most, if not all, Swedish open-hearth steel furnaces are fired with producer gas obtained from wood.

**144. Oil.**<sup>1</sup>—Crude California oil of  $14$ – $17^\circ$  Bé. as a fuel was first used in 1906<sup>2</sup> in the reverberatory furnaces of the Consol. Arizona Smelting Co., Humboldt, Ariz. The furnaces<sup>3</sup> were large having a hearth 98 ft. by 19 ft. 1 in. Each furnace had nine steam-blown burners, three at the end and three on either side, hung by universal connections so that they could be made to point in any direction. The oil was fed under a pressure of 80 lb.; the consumption was from 11 to 19 per cent. of the weight of the charge or from 29 to 52 gal. per ton of ore, and cost delivered in tank cars \$1.25 per barrel of 42 gal. The temperature was higher than that formerly attained with the coal previously used; slags with  $\text{SiO}_2$  48 and CaO 11 per cent. were made, while with coal-firing the highest was  $\text{SiO}_2$  42 per cent. These early favorable results led to the adoption of oil in the Southwest where California oil forms the cheapest fuel. The oil used at present is required to have at  $60^\circ\text{F}$ . a specific gravity of not less than  $13.5^\circ$  Bé.; the density usually is  $14^\circ$  Bé.

Data of some of the leading plants using oil as fuel are given in Tables 51 and 52.

The burners<sup>4</sup> used in copper reverberatory furnaces are all atomizers. Both steam and air serve for producing the spray of the oil. In general, steam is more economical for low pressures up to 10 lb., air for pressures above 10 lb. For the same effect the air-pressure has to be higher than the steam-pressure. Steam, which must be dry, produces a longer flame than does air; with air the oil must be warm ( $80$ – $100^\circ\text{C}$ .) in order to have the desired mobility. A mixture of air and steam has not given favorable results. Most works use a high pressure, as this produces a long flame which melts the charge more quickly than does a shorter flame. Thus, *e.g.*, at Hayden, Ariz., five burners with a pressure of 3 lb. melted only the charge of the first row of feed-hoppers and made the bridge end extremely hot, while three burners and 12 lb. pressure readily melted the charge of the second row of feed-hoppers.

Pressure of steam or air and strength of draft are closely connected. The flame of an oil-burner is short and a clear white. In order to heat a long furnace a strong draft is necessary. Table 55 gives the results of one of the 24-hr. tests with low and high draft, in the oil-fired reverberatory furnace recorded in

<sup>1</sup> Herrick, *Mines and Minerals*, 1910, xxx, 367.

<sup>2</sup> Robinson, *Eng. Min. J.*, 1908, LXXXV, 1064.

<sup>3</sup> Peters, "Principles of Copper Smelting," 1907, p. 210.

<sup>4</sup> Hofman, "General Metallurgy," 1913, p. 330.

Table 55.—TWENTY-FOUR-HOUR TESTS WITH LOW AND HIGH DRAFT AT STEPTOE VALLEY SMELTERY

Dec. 3. Low Draft

Dec. 1, 2, 4, and 5 High Draft

Date	Draft, in. of H <sub>2</sub> O		Total charge, tons	Oil fired, bbl.	Tons charge per bbl. oil	Gal. H <sub>2</sub> O evaporated from and at 212° F.	B.H.P. per boiler	Evap. factor, lb. H <sub>2</sub> O per lb. oil
	Bridge	Verb						
Dec., 1911								
1	0.32	0.95	499	370	1.35	83,853	420	5.57
2	0.30	0.95	503	357	1.41	83,139	418	5.75
3	0.09	0.25	237	220	1.08	50,713	254	5.65
4	0.34	0.90	397	301	1.32	80,124	402	5.75
5	0.34	0.92	466	387	1.20	88,010	440	5.62
Av. high draft, days	0.33	0.93	441	354	1.25	83,780	420	5.84

## Percentage-Analysis of Charge

	Calclines	Seconds	Hot slag	Fettling	Limestone	Flue-dust	Dried concentrates	Grade of matte
1	59.6	15.1	8.0	6.0	11.3	.....	.....	42.9
2	58.3	19.3	6.9	4.0	9.7	1.8	.....	45.6
3	64.5	16.5	.....	5.9	13.1	.....	.....	45.0
4	56.9	24.4	.....	5.3	9.6	3.8	.....	44.9
5	53.2	17.2	9.7	4.7	12.4	2.8	.....	43.6
Av. high draft, days	57.0	19.0	8.1	5.0	10.7	2.8	.....	44.2

## Assay and Analysis of Slag

	Per cent. Cu	Per cent. SiO <sub>2</sub>	Per cent. FeO	Per cent. CaO	Per cent. Al <sub>2</sub> O <sub>3</sub>
1	0.43	43.0	34.8	10.6	7.8
2	0.47	42.2	36.8	9.4	7.3
3	0.40	43.0	35.0	8.9	7.6
4	0.63	43.6	34.7	10.4	8.3
5	0.40	45.0	33.4	9.7	8.3
Av. high draft, days	0.48	43.5	34.9	10.0	7.9

Gallons water evaporated corrected for (1) meter calibration, (2) blowdown, (3) steam pressure and feed-water temperature.

Table 51, carried out by Sørensen in 1911. A comparison of the figures of Dec. 3 (low draft) with the average of Dec. 1, 2, 4, and 5 (high draft) brings out in a striking way the necessity of a high draft.

The continuous feeding of oil makes the fusion of the charge an uninterrupted operation with the result that an oil-fired furnace has a greater smelting-power than when coal is used as fuel; on account of the higher temperature obtained, a slag with a higher percentage of SiO<sub>2</sub> can be made, *e.g.*, 45 per cent., necessitating a correspondingly smaller amount of flux. A record run of 24 hr. made at Steptoe Valley smelter, <sup>1</sup> with the furnace given in Table 51, was 666 tons of charge (60.1 per cent. calcines, 16.8 seconds, 9.0 hot converter slag, 3.9 fettling, 9.6 limestone, 0.6 flue-dust); there was consumed 1 bbl. oil for 1.58 tons of charge or 0.63 bbl. oil per ton (=18.60 per cent. coal per ton charge); the slag made showed SiO<sub>2</sub> 44.0, FeO 44.1, CaO 8.6, Al<sub>2</sub>O<sub>3</sub> 7.4, Cu 0.40 per cent., with an O-ratio of 2.72 with Al<sub>2</sub>O<sub>3</sub> figured as acid; the matte produced contained Cu 40.4 per cent.

Forcing a furnace means a high repair account, for it has to be repaired every three or four months; but with slower work, 300 tons in 24 hr. with a

<sup>1</sup> Mathewson, *Tr. A. I. M. E.*, 1912, XLIV, 781.

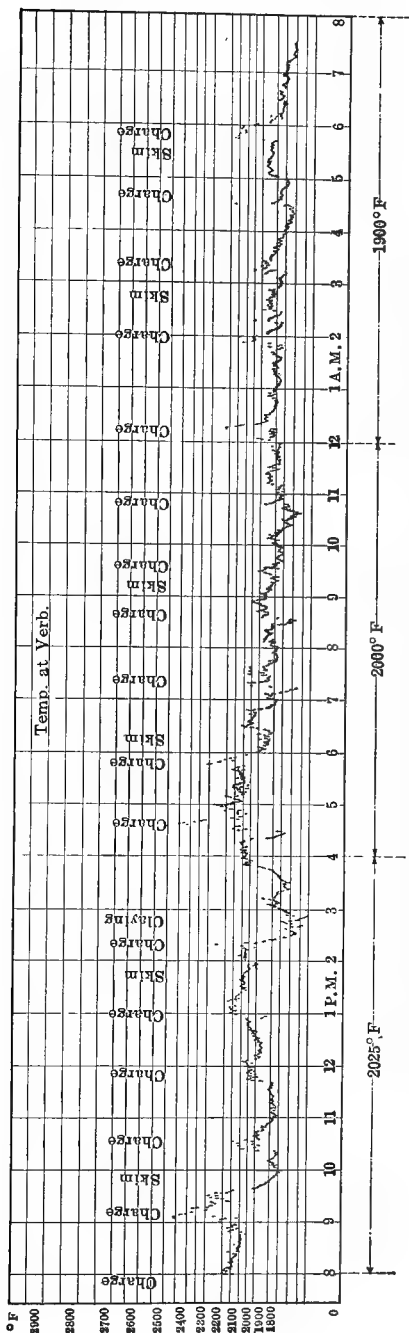
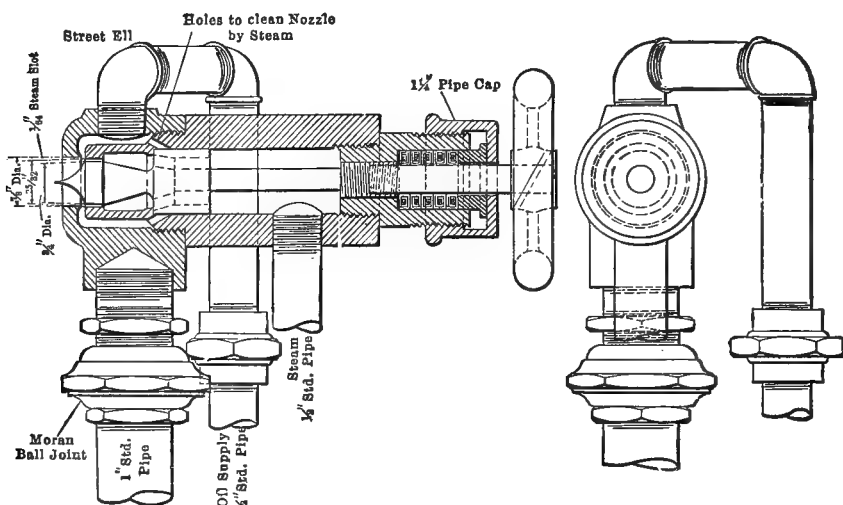


FIG. 307.—Temperature-record of reverberatory matting furnace of Steptoe Valley Smelter.

hearth  $100 \times 19$  ft., the furnace lasts six to seven months. For the same reason the distance between roof and floor has to be greater with the oil- than with the coal-fired furnace, viz.,  $6-7\frac{1}{2}$  vs. 5 ft.

In Fig. 307 is represented a temperature-record taken at the vulcatory or verb of an oil-fired reverberatory furnace of the Steptoe Valley smeltery. About



FIGS. 308-309.—Shelby oil-burner, original.

every hour there are dropped about 14 tons of charge near the firing-end of the furnace, which causes the temperature to fall; skimming and claying have similar effects.

The burners used in matting reverberatories have various forms, each smeltery having developed a type that suits best its own purposes. Two may serve as examples.

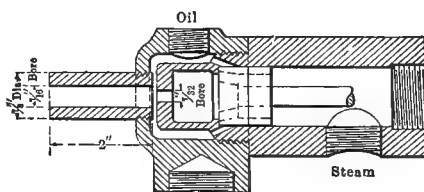


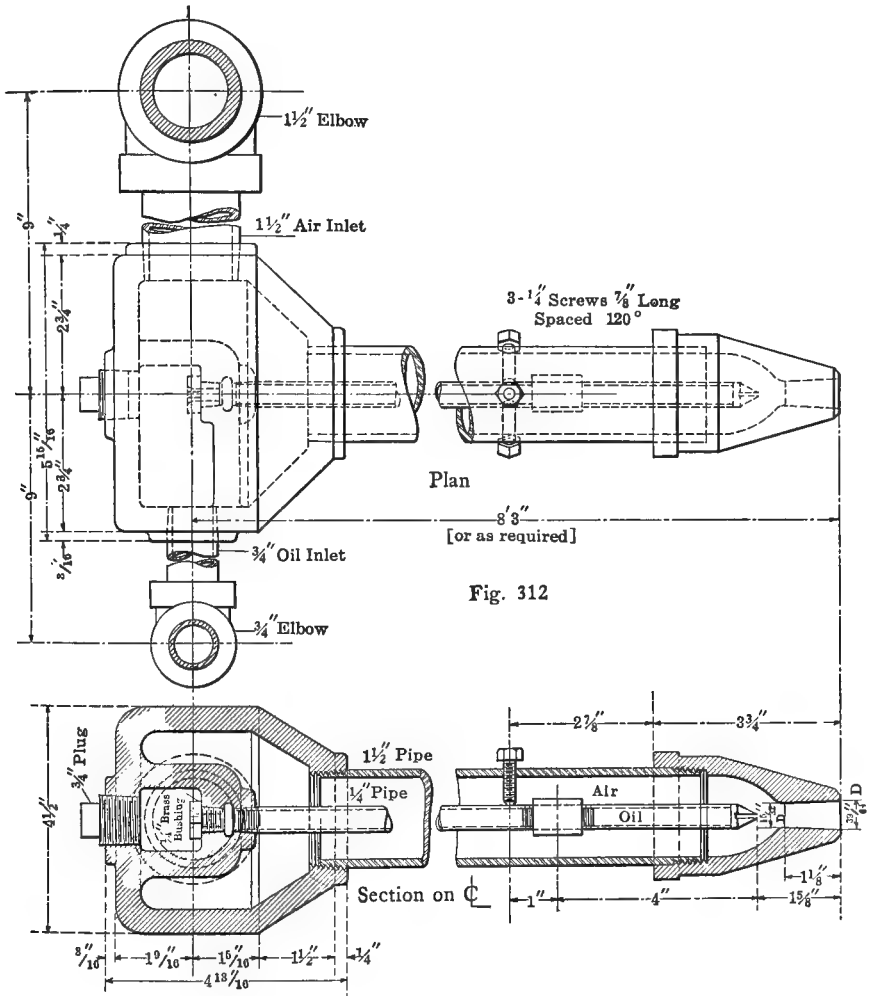
FIG. 310.—Shelby oil-burner, modified.

THE SHELBY BURNER of the Cananea Smeltery,<sup>1</sup> is shown in Figs. 308-310. It is an atomizing burner of the chamber type using steam, mounted on a Moran ball-joint. The oil enters, at 40-lb. pressure, an annular chamber which has an orifice  $\frac{7}{8}$  in. in diameter. There it meets steam of 125 lb. pressure which issues through an annular opening  $\frac{1}{4}$  in. wide ( $\frac{2}{3}$  in. outer and  $\frac{3}{4}$  in. inner diameter) at right angles to the flow of the oil. The flow of steam is regulated by a needle-

<sup>1</sup> *Eng. Min. J.*, 1910, LXXXIX, 31.



valve with rod held by a screw-thread and moved by a hand-wheel. In Fig. 310 a simpler form of nozzle is shown which throws the flame farther into the furnace; the steam-inlet has been changed from the original ring form to a cylindrical port of  $\frac{7}{8}$  in. bore; atomized oil and steam pass through a pipe  $\frac{7}{8}$  in. inner and  $\frac{7}{8}$  in. outer diameter. A burner handles 50-60 bbl. oil in 24 hr.,



FIGS. 311-312.—Sørensen oil-burner, high-pressure air.

requires 0.3-0.4 lb. steam per lb. of oil excluding the  $2\frac{1}{2}$  per cent. which it consumes.

THE SÖRENSEN BURNER OF THE STEPTOE VALLEY SMELTERY is also an atomizing burner and uses high-pressure air. It is shown in Figs. 311-312. A  $\frac{1}{4}$ -in. oil-pipe with conical nozzle is held in position by three adjusting screws in a  $1\frac{1}{2}$ -in. air-pipe provided with a flaring nozzle. The general arrangement of the

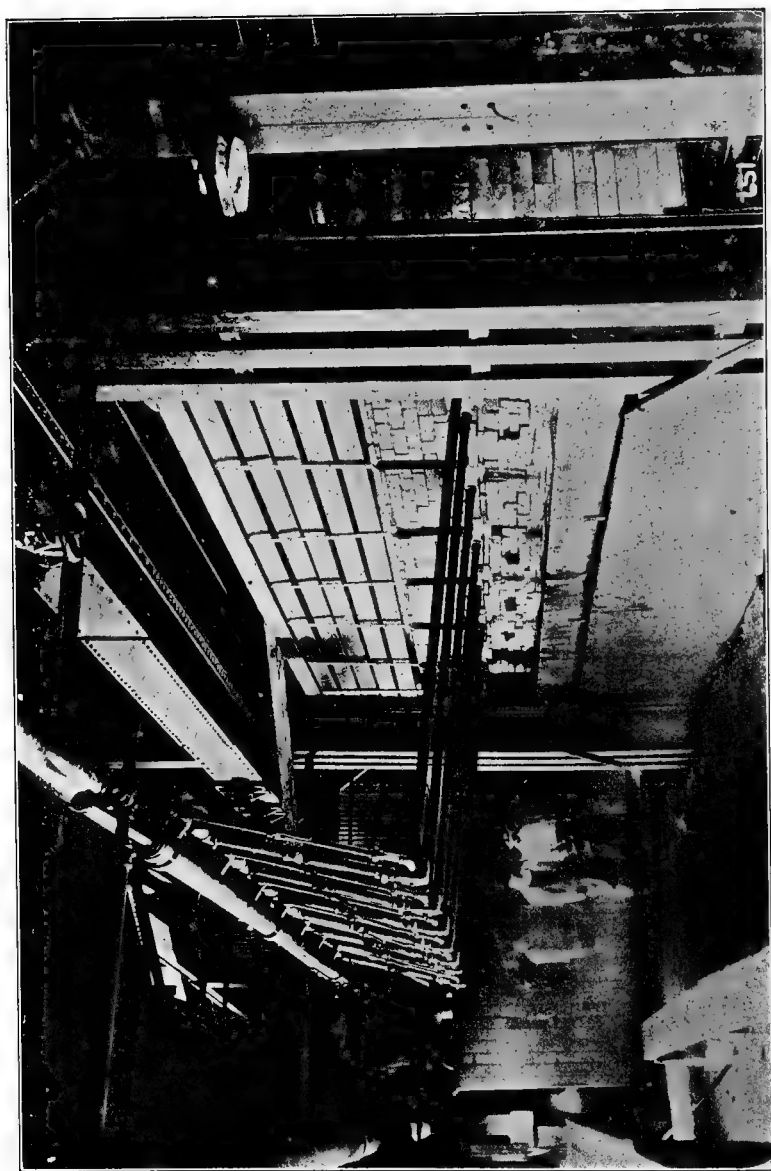


FIG. 313.—Firing-end of Steptoe Valley reverberatory matting furnace.

suspended pipes at the Steptoe furnaces is shown in Fig. 313. Above the burner-ports the bricks are laid so as to leave open vertical slits through which air is to enter in order to furnish additional oxygen, but they very soon become more or less slagged over. The seven pipes of the furnace have burnt in 24 hr. 421 bbl. oil, or 60 bbl. per burner, at an air-pressure of 15 lb.

**145. Slag.**—The slags produced in reverberatory furnaces are nearly always more acid than those in blast-furnaces; they may also differ considerably in constitution. In the blast-furnace all the  $\text{SiO}_2$  must be combined with bases to form a fluid slag; in the reverberatory furnace this is not necessary, as the slag can be and is drawn off, and need not be run off. Slags low in Cu are made, consisting of a moderately fusible silicate-mixture as matrix, holding in suspension particles of quartz, which readily separate from the matte. The Welsh slag (Table 51) given by Le Play as containing  $\text{SiO}_2$  60.5 per cent. is such a porphyritic slag, 30 per cent. is combined and 30.5 per cent. free  $\text{SiO}_2$ . Such slags used to be made more frequently than at present, when the desire for increased smelting power is attained more by high temperatures with completely fluxed  $\text{SiO}_2$  than by a saving of fuel accompanied by a porphyritic slag. All reverberatory furnace slags must be acid in order to avoid rapid corrosion of the siliceous furnace-lining<sup>1</sup> and quick cooling; they must be moderately fusible so as not to require too much fuel or time in forming; they must not be too fluid, as this hinders skimming, nor too viscid, as this prevents matte from settling; finally, the specific gravity ought not to be too high, as it would hinder the separation of matte. All slags, then, run high in  $\text{SiO}_2$ , usually not above  $\text{SiO}_2$  45 per cent., rarely below  $\text{SiO}_2$  36 per cent.; the percentage of CaO used to be lower than is the case to-day. Examples are given in Tables 51 and 52.

Fulton<sup>2</sup> has investigated the constitutions, melting-points, and fluidities of some reverberatory slags made in matting copper ores. The work embodies three series of experiments with three basal slags of the compositions given in Table 56. The slags forming the bases of series I and II run high in  $\text{Al}_2\text{O}_3$ ;

TABLE 56.—COMPOSITIONS OF BASAL REVERBERATORY SLAGS.—(FULTON)

Number of series	Composition				Ratio of $\text{SiO}_2 : \text{FeO} : \text{Al}_2\text{O}_3$
	$\text{SiO}_2$	$\text{FeO}$	$\text{Al}_2\text{O}_3$	CaO	
	Per cent.	Per cent.	Per cent.	Per cent.	
I.....	42.65	36.12	11.30	6.20	377 : 319 : 100
II.....	44.50	38.20	11.85	5.10	376 : 323 : 100
III.....	44.30	43.1	4.85	6.80	914 : 888 : 100

those of series I–III contain increasing amounts of FeO. In each series the percentage of CaO has been increased and the silicate degree correspondingly decreased. Table 57 gives the numerical results of the experiments in series I, and Fig. 314 the plot; Table 58 stands for series II and Fig. 315 for the plot; Table 59 for series III and Fig. 316 for the plot.

<sup>1</sup> The magnesite lining of Copper Cliff forms the exception.

<sup>2</sup> *Tr. A. I. M. E.*, 1912, XLIV, 751.

TABLE 57.—COMPOSITIONS AND MELTING-POINTS OF SERIES I OF FULTON'S REVERBERATORY SLAGS

Number	Composition					Silicate, degree	Melting- point, deg. C.
	SiO <sub>2</sub>	FeO	CaO	Al <sub>2</sub> O <sub>3</sub>	Total		
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.		
1	42.65	36.12	6.20	11.30	96.37	1.40	979
2	40.66	34.33	10.80	10.70	96.49	1.28	1011
3	38.80	32.60	14.95	10.02	96.37	1.19	1060
4	36.90	31.10	18.52	9.75	96.27	1.09	1081
5	35.40	29.65	22.12	9.35	96.52	1.02	1137
6	33.92	28.48	25.14	9.00	96.54	0.96	1151

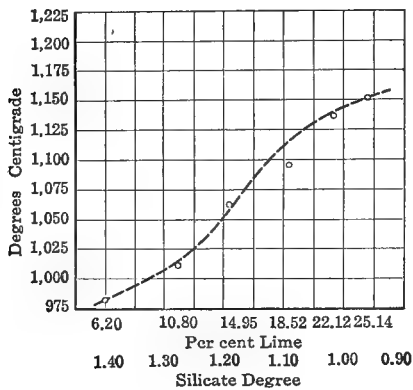


FIG. 314.—Melting-point curve, first series, Table 57.

TABLE 58.—COMPOSITIONS AND MELTING-POINTS OF SERIES II OF FULTON'S REVERBERATORY SLAGS

Number	Composition					Silicate degree	Melting- point, deg. C.
	SiO <sub>2</sub>	FeO	CaO	Al <sub>2</sub> O <sub>3</sub>	Total		
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.		
1	44.50	38.20	5.10	11.85	99.65	1.51	1050
2	44.00	37.80	6.14	11.73	99.67	1.48	1025
3	43.50	37.30	7.15	11.60	99.55	1.45	988
4	43.20	37.00	8.16	11.51	99.87	1.42	982
5	42.25	36.20	10.04	11.23	99.72	1.38	1010
6	40.50	34.65	13.60	10.75	99.50	1.28	1054
7	38.90	33.25	16.80	10.40	99.35	1.20	1091
8	37.55	32.10	19.90	10.05	99.60	1.13	1103
9	36.20	30.80	22.56	9.67	99.30	1.06	1107

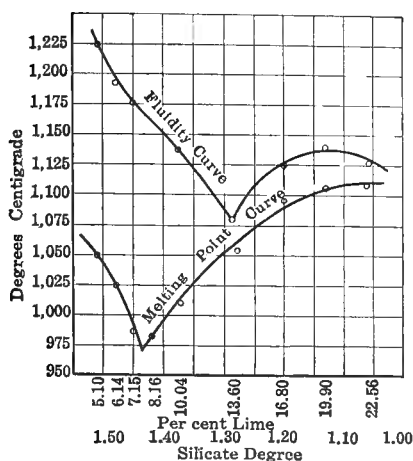


FIG. 315.—Melting-point and fluidity curves, second series, Table 58.

TABLE 59.—COMPOSITIONS AND MELTING-POINTS OF SERIES III OF FULTON'S REVERBERATORY SLAGS

Number	Composition					Silicate degree	Melting-point, deg. C.
	SiO <sub>2</sub>	FeO	CaO	Al <sub>2</sub> O <sub>3</sub>	Total		
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.		
1	44.30	43.10	6.80	4.85	99.05	1.66	1000
2	42.65	41.51	10.29	4.69	99.14	1.54	1010
3	41.11	40.01	13.53	4.51	99.16	1.44	1034
4	38.34	37.22	19.35	4.21	99.12	1.27	1097
5	35.92	34.97	24.43	3.94	99.26	1.13	1167
6	33.79	32.89	28.92	3.71	99.31	1.03	1207
7	31.90	31.05	32.90	3.50	99.35	0.934	1186

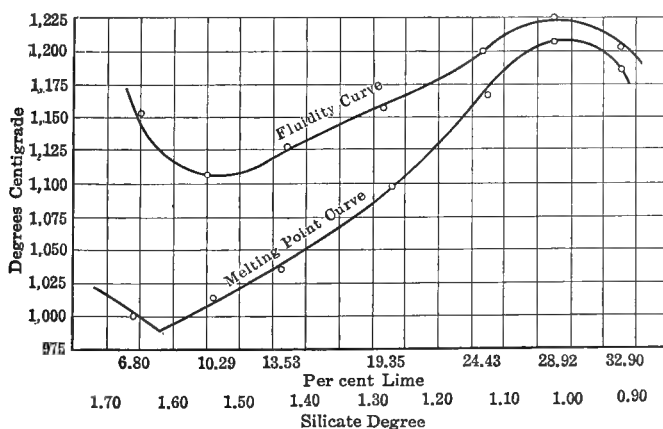


FIG. 316.—Melting-point and fluidity curves, third series, Table 59.

In Figs. 315 and 316 the fluidity curves represent the temperatures at which the slags held in platinum crucibles were sufficiently fluid to permit easy stirring with a heavy platinum rod.

Curves in Figs. 315 and 316 are V-shaped; in Fig. 314 the eutectic point was missed. The lowest melting-points of the three curves, Figs. 314-316, lie between silications 1.4-1.65, depending upon the character of the several bases. Fig. 314 shows that in a highly aluminous slag an increase of CaO alone causes a rise in the melting-point; this confirms the experience in practice of having to raise both the SiO<sub>2</sub>- and CaO-content for the lowering of the melting-point. The curve in Fig. 315, which covers a higher range of SiO<sub>2</sub>-content (44.50-36.20 per cent.) than the curve in Fig. 314 (42.65-33.92 per cent.), shows that an addition of CaO lowers the melting-point until a minimum has been reached as was to be expected. The curve in Fig. 316, beginning with a lower percentage of SiO<sub>2</sub> than in Fig. 315 (44.30 *vs.* 44.50), reaches the lowest melting-point earlier.

**146. Chemistry.**<sup>1</sup>—It has been stated in § 127 that in the copper reverberatory furnace S was the reducing agent. The main reactions as regards Cu are reduction by means of S, and sulphurization by means of FeS; and as regards the gangue, slagging in a partially oxidizing atmosphere.

REDUCTION OF CU may be expressed by  $\text{Cu}_2\text{S} + 2\text{CuO} = 4\text{Cu} + \text{SO}_2$ ;  $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} = 6\text{Cu} + \text{SO}_2$ ;  $\text{Cu}_2\text{S} + 3\text{CuO} = 3\text{Cu} + \text{Cu}_2\text{O} + \text{SO}_2$ ;  $\text{Cu}_2\text{S} + 6\text{CuO} = 4\text{Cu}_2\text{O} + \text{SO}_2$ . The first two reactions<sup>2</sup> begin at about 500° C., and all SO<sub>2</sub> is set free at 1000°.

SULPHURIZATION may be formulated by  $2\text{Cu} + \text{FeS} \rightleftharpoons \text{Cu}_2\text{S} + \text{Fe}$ ;  $\text{Cu}_2\text{O} + \text{FeS} = \text{Cu}_2\text{S} + \text{FeO}$ ;  $6\text{CuO} + 4\text{FeS} = 3\text{Cu}_2\text{S} + 4\text{FeO} + \text{SO}_2$ ;  $\text{Cu}_2\text{SiO}_3 + \text{FeS} = \text{Cu}_2\text{S} + \text{FeSiO}_3$ ;  $\text{Cu}_6\text{Si}_3\text{O}_{12} + 4\text{FeS} = 3\text{Cu}_2\text{S} + \text{Fe}_4\text{Si}_3\text{O}_{10} + \text{SO}_2$ .

The recent investigations of Juschewitsch<sup>3</sup> having established the formation of the compound (Cu<sub>2</sub>S)<sub>2</sub>.FeS in a pyrometallurgical process, the reactions between Cu<sub>2</sub>S, Cu<sub>2</sub>O and Fe, FeS assume the following forms:  $(\text{Cu}_2\text{S})_2.\text{FeS} + 2\text{Cu} = 3\text{Cu}_2\text{S} + \text{Fe}$ ;  $2\text{Cu}_2\text{O} + 3\text{FeS} = (\text{Cu}_2\text{S})_2.\text{FeS} + 2\text{FeO}$ ; and  $12\text{CuO} + 10\text{FeS} = 3(\text{Cu}_2\text{S})_2.\text{FeS} + 7\text{FeO} + \text{SO}_2 + 3\text{O}$ .

The decomposition of CuO by Fe according to Friedrich<sup>4</sup> begins at about Bases 740° C.

REDUCTION OF IRON OXIDE may be expressed by  $3\text{Fe}_2\text{O}_3 + \text{FeS} = 7\text{FeO} + \text{SO}_2$ ;  $\text{Fe}_2\text{O}_3 + \text{Fe} = 3\text{FeO}$ ;  $\text{Fe}_2\text{O}_3 + \text{CO} = 2\text{FeO} + \text{CO}_2$ ;  $\text{Fe}_2\text{O}_3 + \text{heat} + \text{SiO}_2 = 2\text{FeO} + \text{O} + \text{SiO}_2$ ; and slagging by  $\text{FeO} + x\text{SiO}_2 = \text{FeSi}_x\text{O}_{2x+1}$ , and by Other  $+ y\text{SiO}_2 = \text{O}$ .-B. Si<sub>y</sub>O<sub>2y+1</sub>.

As the hot flame impinges upon a newly fed charge, the most fusible parts on the surface will melt first and passing downward will leave new parts exposed to the action of the flame. This goes on until the whole is fused. "Blanket Slag," or slag which forms on the charge and consists of partly fused material,

<sup>1</sup> Laist, *Tr. A. I. M. E.*, 1912, XLIV, 806

<sup>2</sup> Doeltz, *Metallurgie*, 1907, IV, 421.

<sup>3</sup> *Metallurgie*, 1912, IX, 543.

<sup>4</sup> *Stahl u. Eisen*, 1911, XXXI, 2041.

gave Fulton<sup>1</sup> SiO<sub>2</sub> 52.08, FeO 27.96, Al<sub>2</sub>O<sub>3</sub> 9.00, CaO 5.90, MgO 0.23, K(Na)<sub>2</sub>O 1.00 per cent., and SiO<sub>2</sub> 38.68, FeO 38.10, Al<sub>2</sub>O<sub>3</sub> 8.48, CaO 9.92, MgO 0.79, (NaK)<sub>2</sub>O 1.00 per cent. This would not form if the charge components were well mixed, and they usually are not.<sup>2</sup> In the meantime bubbles of SO<sub>2</sub> rise from the pasty parts of the surface; they increase in number and stir up the unmelted and partly melted parts of the charge, which slowly decrease in quantity; matte will collect on the bottom and slag float on the top. The FeS held in solution by the slag sulphurizes any slagged Cu, so that the Cu finally remaining in the slag is present more in the form of a suspended matte-pellet or dissolved matte than of a copper silicate. The Zn and Pb of the charge are partly volatilized, partly matted and scorified; As and Sb are volatilized, matted, and slagged; precious metals are collected in the matte. The records of Gibb<sup>3</sup> show that in smelting roasted sulphide ore with Cu 10.60, As 0.102, Sb 0.025, Bi 0.010 per cent., there was eliminated, As 62.8 per cent., Sb 57.6, Bi 20.2; As and Sb entered the slag, while Bi was expelled mainly by volatilization. Comparing these data with those obtained by a reducing fusion of the same ore in the blast-furnace (p 189), it is seen that the reverberatory removed more As and Sb than the blast-furnace, while the reverse was the case with Bi.

**147. Calculations of Charge.**<sup>4</sup>—The basis of calculation is the same as with the blast-furnace (§ 102, 115), *i.e.*, the kind and quantity of matte and slag that are to be produced. The Cu is calculated as entering the matte a Cu<sub>2</sub>S accompanied by a given amount of FeS, which depends upon the grade of matte desired. It may be assumed that 75 per cent. of the Pb, 50 per cent. of the Zn, and 25 per cent. of the Mn will be found in the matte so that this contains perhaps only 95 per cent. Cu<sub>2</sub>S,  $\propto$  FeS; the remaining constituents of the ore will enter the slag. Some flux, usually limestone, may have to be added to the charge to obtain the right degree of fusibility and fluidity. As the ore charged is fine, there is some loss (2 + per cent.) by dusting; further, in smelting, there is a variable loss of S, which, according to Vivian,<sup>5</sup> in the old Swansea furnaces amounted to 13 per cent., and which, according to more recent observations by Peters<sup>6</sup> causes the matte to run about 8 per cent. higher in Cu than expected. Again, all the SiO<sub>2</sub> may not be scorified, part being carried out by the slag mechanically suspended, especially parts of the charge which are larger than  $\frac{1}{2}$  in. Lastly, the results obtained are governed to a considerable extent by the handling of the furnace. These variables are the reason why preliminary calculations give results which agree only approximately with the figures obtained in actual work. When the necessary factors have been obtained by experience, theory and practice will be in better harmony. Some preliminary factors for the first calculations can be obtained by making crucible fusions to find the quantities and grades of

<sup>1</sup> *Loc. cit.*

<sup>2</sup> See Demond, *loc. cit.*

<sup>3</sup> *Tr. A. I. M. E.*, 1903, XXXIII, 657.

<sup>4</sup> Walker, *Eng. Min. J.*, 1906, LXXXI, 852.

<sup>5</sup> *Eng. Min. J.*, 1881, XXXI, 249.

<sup>6</sup> *Modern Copper Smelting*, 1895, p. 83.

matte collected in the form of buttons, and to form an idea of the fluidity of the slag.

**148. Heat Balance of Reverberatory Matting Furnace at Anaconda.**—The data of the subjoined heat-balance, kindly furnished by Mr. W. Wraith, are the result of an investigation, lasting 101 hours, carried on in 1905 with furnace No. 2. This has a hearth 102 by 19 ft. (area 1807 sq. ft.,) and a grate 7 by 16 ft. (area 112 sq. ft.). There were smelted in 24 hr. 272 tons of material with a ratio of 4.37 tons of material to 1 ton of coal. The assay of the charge gave  $\text{SiO}_2$  26.1,  $\text{FeO}$  40.2,  $\text{CaO}$  2.9,  $\text{Cu}$  9.0,  $\text{S}$  8.1 per cent.

#### SUMMARY OF HEAT DISTRIBUTION

Debit	B.t.u.	Per cent. of total debited heat
Net calorific value of coal consumed.....	5,520,200,000	94.92
Heat in calcine and flue-dust, above atmospheric temperature.	295,500,000	5.08
	5,815,700,000	100.00
<b>Credit</b>		
Heat in slag above atmospheric temperature.....	950,400,000	16.34
Heat in matte above atmospheric temperature.....	184,700,000	3.18
Heat lost by radiation.....	671,900,000	11.55
Heat to air drawn through bridge-plate.....	9,020,000	0.16
Sensible heat in droppings from grate above atmospheric temperature.	45,330,000	0.78
Heat in steam from boilers.....	1,908,380,000	32.81
Heat in gases escaping beyond boilers.....	766,800,000	13.18
	4,536,530,000	78.00

There have been accounted 78.0 per cent. of the heat with which the furnace is debited; the remaining 22 per cent. have to be sought in the heat which passed into the ground, and the heat due to slag-formation.

A striking feature is the fact that only 19.52 per cent. of the heat is found in the slag and matte, while the two waste-heat boilers saved 32.81 per cent. developing 567 h.p. The calcines which entered the furnace with a temperature of  $950^\circ\text{F}$ . form 5.08 per cent. of the heat with which the furnace is debited. Considering that only 19.52 per cent. of the total heat appear in the slag and matte produced, the evidence is furnished that  $5.08 : 19.52 \times 100 = 26$  per cent. more coal and time would be required if the calcine had been at atmospheric temperature.<sup>1</sup> The case actually would be more unfavorable if the manner in which a cold charge balls up in the furnace is considered.

**149. Management.**<sup>2</sup>—Formerly all reverberatory ore-smelting furnaces

<sup>1</sup> See Demond, *loc. cit.*

<sup>2</sup> Lloyd, *Eng. Min. J.*, 1904, LXXVII, 716.

Peters, *Metallurgie*, 1905, II, pp. 35, 63.

Offerhaus, *Eng. Min. J.*, 1908, LXXXV, 1189, 1234.

Moore, *op. cit.*, 1910, LXXXIX, 1021, 1063.



received their entire charges at stated periods ranging from 4 to 8 hr.; a charge was smelted, the slag drawn, and the matte tapped completely or only in part. Since the advent of the 100-ft. furnaces at Anaconda, this periodical charging of large quantities has been changed into feeding relatively small amounts at intervals of 20 to 60 min. as is common in still shorter periods with the blast-furnace. The second method, which is a radical departure from the first, is becoming the general practice in ore-smelting as fast as large furnaces are replacing the smaller.

*a. FEEDING LARGE CHARGES AT LONG INTERVALS.*—Presupposing the hearth to have been emptied, the charge is dropped from the hoppers in the roof. Roasted concentrates (calcines) are charged hot, whenever this is possible, and the fluxes added while charging calcines. If the charge is to be made up in the furnace, an undesirable procedure,<sup>1</sup> siliceous ore will be dropped first, the roasted ore next, and lastly foul slag. In a non-regenerative furnace the bulk of the charge is collected near or at the fire-bridge; in regenerative furnaces near or at the ends. If the desired distribution of charge cannot be effected through the hoppers, the charge will have to be spread by hand. After charging, the doors are closed and luted, and the fire is urged. A strong steady heat is essential for quick smelting. The flame at first will soften readily-fusible components of the charge; these will sink and expose others to the high temperature of the furnace; matte will collect on the bottom and carry slag and unmelted parts of the charge. At intervals these will be rabbled from the skimming door, the bottom will be scraped to detach adhering lumps and to float them to the surface that they may be liquefied. If the bottom feels rough and gritty instead of smooth and soapy, firing has to be continued, as the fusion is not completed. With a zinky charge it is essential to have the furnace especially hot toward the end of the fusion in order that mushy zinky matte which on account of its low specific gravity floats on top of the normal matte may separate completely from the slag. When a charge has been smelted, the slag will be rabbled to set free particles of matte which may have remained entangled. In order to free slag from scorified Cu, pyrite has been sprinkled over it; in a similar manner CuO has been introduced to have it react with FeS dissolved in the slag, then the matte formed in its passage downward through the slag reduces the silver-content; at Argo, Colo., 75 per cent. of the Ag of the slag has been thus recovered. When fusion is completed and matte well separated from the slag, the skimming door is opened, perhaps also a working door, for a short time, to cool and stiffen the slag. The slag is skimmed into an overflow slag pot to collect any particles of matte that have been accidentally drawn out; the overflowing clean slag is collected in waste-slag pots and hauled to the dump or granulated. In former times, with smaller furnaces than used in recent years, a series of basin-shaped molds was formed in a sand bed beneath the skimming doors; the slag was drawn into the mold beneath the door and allowed to overflow into the neighboring molds after breaking down the sand ridges separating the molds in order to form communicating channels. In the mold beneath the door was collected any matte drawn out with the slag; the "plate slag" floating on top of the matte

<sup>1</sup> See Demond, *loc. cit.*

was resmelted, perhaps also the cake on either side, as they contained pellets of matte. When the slag has been removed, the matte-tap is opened and the out-flowing matte collected in sand molds built along the side, or in cast-iron molds having overflow lips. Sometimes the matte is granulated by allowing a heavy jet of water to impinge upon it when it runs in a thin stream from the spout. The granules are collected in a deep basin from which the combined granulating and cooling water flows through shallow settling tanks to collect floating par-particles. When the furnace has been emptied any damage to the hearth and the fettling is repaired before the next charge is introduced.

Most furnaces were tapped dry after every second or third charge; at Argo, Colo., the matte-fall was so small that twenty-four and more charges were smelted before the matte was removed for further treatment. This holding of a bath of matte in the furnace is accompanied by so many advantages that it has become the common practice even in cases when the matte is to be shipped cold instead of going in the liquid state direct to the converter. With converting plants, the reverberatory furnace forms a reservoir for matte, forming a bed 3-14 in. deep, as does the settler of the blast-furnace (p. 169). As long as the furnace construction is strong, the bottom built up solid, the connection between sand-bottom and side wall made secure, there is no danger of matte getting beneath the sand-bottom and causing trouble. Such a mass of loosened furnace-bottom, "floater," gave upon analysis<sup>1</sup>  $\text{SiO}_2$  84.62,  $\text{FeO}$  8.53,  $\text{Al}_2\text{O}_3$  2.13,  $\text{CaO}$  0.90,  $\text{MgO}$  trace,  $\text{K}(\text{Na})_2\text{O}$  1.00 per cent. The advantages of having a bath of matte on the hearth are: It prevents corrosion of the bottom, as basic constituents of the charge do not come in contact with it; it reduces the repair of the fettling from say once a day to once a month, because the slag line can be held at about the same level; it diminishes the repair of the furnace, as the temperature can be kept more even; it does away with the labor required for spreading the charge, or greatly reduces it; it diminishes the loss of heat, as the side doors need to be opened very little; it increases the smelting power by the reduced necessity of cooling the furnace and by the more rapid fusion of the charge when floating upon hot matte than when resting upon a partly cooled bottom.

With all these improvements in the mode of operating, the dropping of large charges at long intervals has the drawback that the furnace, say 50 by 20 ft., is cooled considerably when it receives from 15 to 20 tons of charge every 4 or 5 hr.; much time is taken up to bring the furnace up to the required temperature, and less time is given to actual smelting. Fig. 317 gives a chart showing the variations of temperature in smelting in an Anaconda ore-furnace of 1903. When the furnace had reached its maximum heat of  $2750^\circ\text{F}$ . at 10.40, and the new charge had been dropped and leveled, the temperature fell to  $2150^\circ\text{F}$ . at 11.00; it now took from 11.00 to 2.15 to gradually raise the temperature which reached  $2850^\circ\text{F}$ . when the fusion was completed. The introduction of the new charge caused the temperature to fall  $550^\circ\text{F}$ ., whereupon the heating-up had to be begun again. The depressions in the curve also bring out clearly the falls of temperature caused by stoking (indicated by  $\circ$ ) and rabbling.

<sup>1</sup> Fulton, *Tr. A. I. M. E.*, 1912, XLIV, 751

If the time wasted in heating to fusion temperature can be saved, the smelting power is greatly increased. This is attained by feeding small charges frequently.

*b. FEEDING SMALL CHARGES AT SHORT INTERVALS.*—This was first developed by E. P. Mathewson at Anaconda.<sup>1</sup> The furnace, Figs. 272–274, has two ore-hoppers discharging into four openings in the roof near the fire-bridge, and four coal-hoppers with corresponding openings in the roof above the fire-box. Before dropping a charge, a side door near the ore-hoppers is opened; and a rabble inserted to ascertain whether there remains any unfused material (“floaters”). This is moved toward the fire-bridge<sup>2</sup> and fused, or a pipe pushed underneath it

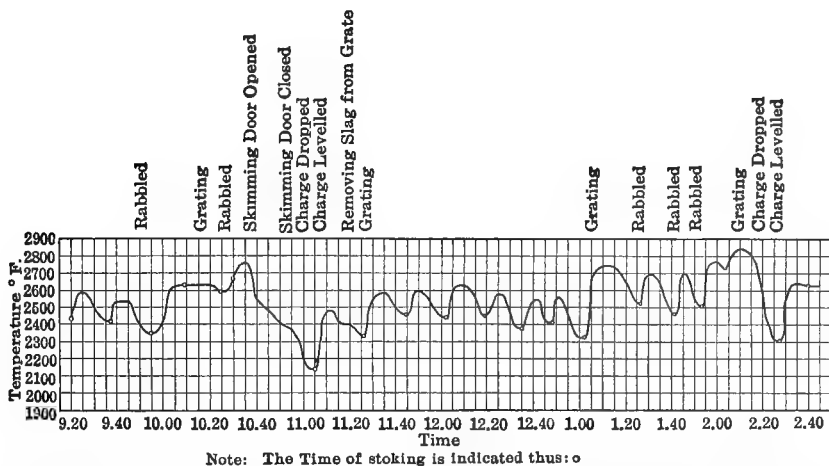


FIG. 317.—Variations in temperature of Anaconda reverberatory matting furnace, fed with large charges.

and air forced through so that conversion of matte furnishes the heat and the base necessary to flux the siliceous floater. Now 10 tons of charge are dropped from the first and 5 tons from the second hopper. The charge falls upon a bath of not less than 3 or 4 in. of matte covered by about 8 in. of slag, spreads more or less, and moves downward toward the flue, at first in two streams. In this way 15 tons of charge are dropped into the furnace every 80 min. In the same manner 3000 lb. of coal are dropped every 40 min. into the fire-place through four openings, the level of the coal being ascertained by feeling with a rod through openings in the side. The temperature in the furnace is pretty uniform as shown in Fig. 318, the highest being 1550° C.; the temperature of the slag as it leaves the furnace is 1120° C.; that of the gas 1060° C.;<sup>3</sup> depressions in temperature caused by feeding of charges are not shown; they resemble those given in Fig. 307.

<sup>1</sup> Austin, *Tr. A. I. M. E.*, 1906, XXXVII, 470.

Offerhaus, *Eng. Min. J.*, 1908, LXXXV, 1191, detail records.

<sup>2</sup> Editor, *Eng. Min. J.*, 1911, XCI, 1243.

<sup>3</sup> Other measurements of furnace- and slag-temperatures: Clevenger, *Mel. Chem. Eng.*, 1913, XI, 447.

Slag is skimmed every 4 hr.; between skimming and dropping of last charge there is left an interval of 40 min.; the skimming door is removed, the sand-dam cut open, and the slag allowed to run out into a settling-trough 7 by 24 ft. and 18 in. deep, when the overflowing waste slag is granulated. The flow of slag is regulated by a rabble (blade 5×9 or 6×16 in., handle 12 ft.); from 40 to 60 tons of slag are thus drawn in from 15 to 20 min. When the furnace is filled with matte, *i.e.*, with about 200 tons, part is tapped as needed by the converting department.

The grating is done every 4 hr. and takes from 35 to 45 min.; the clinkers on the grate are broken up with heavy bars and removed; those on the bridge, likely to be very hard, are attacked at the same time. A good deal of fine coal falls through the grate spaces (grate, 2 in. square, space 6 in.), especially in grating. Clinkers and ashes are removed by a stream of water, and pass over a

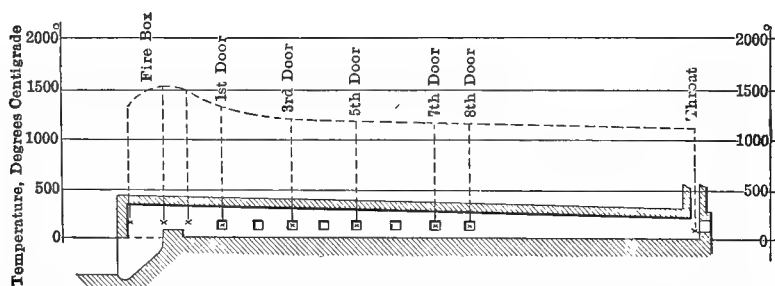


FIG. 318.—Temperature-curve of Anaconda reverberatory matting furnace, fed with small charges.

grizzlie, the oversize going to waste and the undersize to jigs which recover about 10 per cent. coal and coke to be incorporated in the flue-dust briquetting mixture (§ 122) of the blast-furnace.

Claying, or repairing the fettling, at Anaconda is confined mainly to the proximity of the fire-bridge. It has to be done once a month, the necessity for it being indicated by the conker-plate becoming red hot. When claying is contemplated, the furnace is gotten ready by allowing the matte to rise to the level of the skimming plate, skimming the slag clean, tapping the 200 tons of matte into twenty ladles holding from 7 to 10 tons each; this takes several hours. Two or three doors are opened on each side near the fire-bridge, and about 20 tons of self-baking sand ( $\text{SiO}_2$  95 per cent.) thrown in during the operation.

At Cananea<sup>1</sup> the device of Gmahlin-Shelby, Fig. 319, is in successful operation in the 100×19-ft. oil-fired furnace (Figs. 279–287). In the roof, extending the length of the furnace, are openings, 5 by 5 in. and 18 in. apart, which are covered by fire-brick made air-tight with fine ore. Above the furnace is a traveling hopper for distributing the fettling material, fine siliceous ore which has been

<sup>1</sup> Ricketts, *Tr. Inst. Min. Met.*, 1909–10, XIX, 160; *Min. World*, 1909, XXXI, 1116; *Eng. Min. J.*, 1910, LXXXIX, 317.

moistened. Every day some of the fettling is dropped through the holes in places where it is needed; it trickles down over the side walls, which are built with a slight batter, and forms a bank to be tamped down gently. Thus every day from 10 to 15 tons of siliceous ore are fed and smelted; the level of the slag line is kept in repair; and the furnace work need not be stopped for claying.

At the Garfield plant and other works this method of claying has also proved very satisfactory. In fact, the temporary shutting down of a furnace causes the

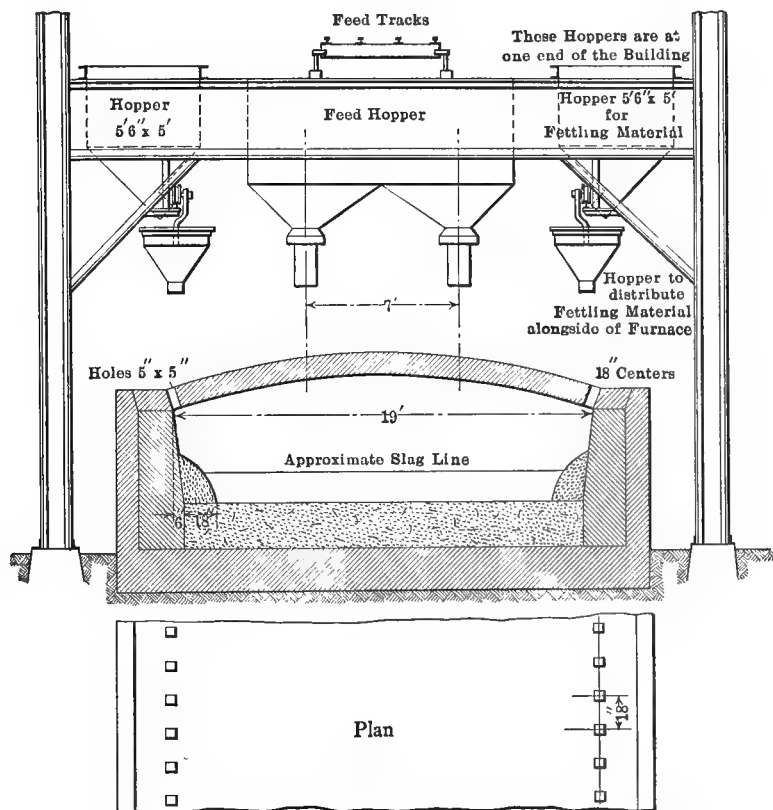


FIG. 319.—Gmahlin-Shelby fettling apparatus at Cananea.

brick in the roof to become loose and not form tight joints again when smelting is started; hence air leaks into the furnace. It has been proved that with this continuous claying the smelting power of the furnace is increased and the fuel consumption decreased.

Automatic records of the different operations (charging, skimming, tapping, etc.) as carried out one after the other may be kept by recorders of the Bristol type.<sup>1</sup>

<sup>1</sup> Jager, *Eng. Min. J.*, 1909, LXXXVII, 1240.

**150. Accessory Apparatus, Products, Losses, Cost.**—The accessory apparatus such as ladles for slag and matte are the same as with the blast-furnace (§ 95, 96).

THE PRODUCTS, matte, slag, and flue-dust are similar (§ 118 and foll.). At Argo, Colo.,<sup>1</sup> the ore-slag from the reverberatory furnace, with hearth 42 by 19 ft., was skimmed or tapped into a launder delivering into a smaller reverberatory furnace, with hearth 20 by 14 ft., and a small amount of pyrite added to clean the ore-slag. The ore-furnace treated a 12-ton charge in 3.5 hr., and the ore-slag remained the same length of time in the cleaning furnace.

THE LOSSES of Cu in reverberatory slags are usually greater than those in the slags of blast-furnaces; they range from 0.3 to 0.5 per cent. Cu. By using the blast-furnace settler with the reverberatory furnace, as is the case with some furnaces at Great Falls, Mont.,<sup>2</sup> the slag-loss in the reverberatory has been reduced to the figure of that of the blast-furnace. At Anaconda with the Mathewson reverberatory furnace the slag-loss<sup>3</sup> is only 0.30–0.35 per cent. Cu owing to the long path that the slag has to travel before it is tapped.

THE COST of smelting has been greatly reduced in recent years. The official statements of 1903<sup>4</sup> made the cost at Butte, Mont., \$3.40–3.60 per ton of ore; with the saving of some of the waste heat this figure is reduced to about \$2.50; with the new Anaconda furnace the cost is about \$1.50 per ton of ore. Cananea<sup>5</sup> smelts for \$1.40–1.77 according to the character of the charge;<sup>6</sup> Utah Consolidated<sup>7</sup> for \$1.40. An analysis of the cost of smelting at the Bingham works, now closed, is made by Barbour.<sup>8</sup> Moore<sup>9</sup> gives the costs of total treatment of 1 ton of ore from ore to blister copper as shown in Table 60.

TABLE 60.—COST OF SMELTING IN REVERBERATORY FURNACE AND OF CONVERTING RESULTING MATTE

Smeltery	Fuel	Power	Labor	Sup- plies and re- pairs	Sal- aries	Lab- ora- tory	Gen- eral ex- penses	Sam- pling	Roast- ing	Con- vert- ing	Flux and fet- tling	Total
Cananea....	\$0.91	0.02	0.23	0.36	0.08	....	.....	.....	0.17	0.68	0.08	\$2.53
Garfield....	0.91	0.02	0.37	0.13	0.04	0.02	0.19	0.22	0.22	0.50	0.03	2.65

**151. General Arrangement of MacDougall and Reverberatory Plant, Copper Queen Consolidated Mining Co.**—A plan of the new roasting and rever-

<sup>1</sup> H. N. Pearce, *Tr. A. I. M. E.*, 1906, xxxvi, 891.

<sup>2</sup> *Eng. Min. J.*, 1906, lxxxix, 92.

<sup>3</sup> *Eng. Min. J.*, 1908, lxxxv, 1237.

<sup>4</sup> *Eng. Min. J.*, 1903, lxxv, 708.

<sup>5</sup> Ricketts, *loc. cit.*; *Eng. Min. J.*, 1911, xcii, 694.

<sup>6</sup> *Eng. Min. J.*, 1911, xci, 1252.

<sup>7</sup> Austin, *Min. Sc. Press*, 1911, cii, 178.

<sup>8</sup> *Eng. Min. J.* 1911. xci, 1252.

<sup>9</sup> *Op. cit.* 1910, lxxxix, 1065.

beratory smelting divisions of the Copper Queen Consolidated Mining Co., at Douglas, Ariz., is shown in Fig. 320. The plant went into operation in 1912. The plan shows six MacDougall roasting furnaces, 18 ft. in diameter (see page 110) arranged in two rows. The gases pass with a velocity of 3 ft. per second into the elevated dust-chamber, built of hollow brick on a steel frame; these chambers are provided with Roesing wires (§ 122) where they drop their dust, to be returned to the roasting-furnace charges, before they enter the central stack. This also furnishes the draft for the two oil-fired reverberatory smelting furnaces in operation.

The roaster charge is so made up that the calcine can go direct without further additions to the reverberatory furnaces, where it is delivered on the elevated calcine tracks. The reverberatory-furnace gases, after passing through boilers and economizers, are collected in a dust-chamber and then enter the central stack. Beneath the throats of the furnaces is a tunnel in which travel the

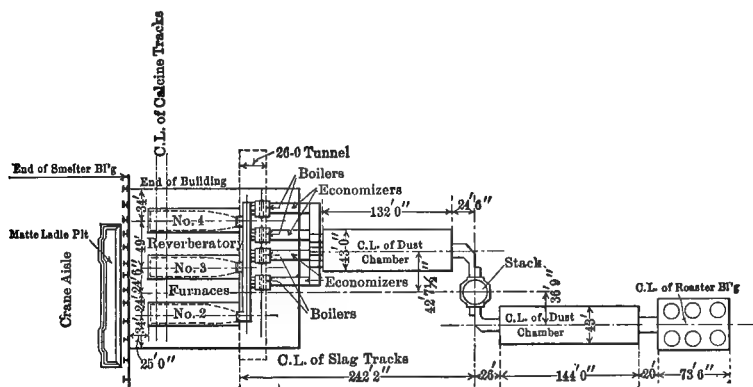


FIG. 320.—Plan of new roasting and reverberatory-smelting departments at the Copper Queen Works.

waste-slag pots; at the firing-end is the matte-ladle pit, the ladles of which are handled by the same cranes that manipulate the ladles of the ten blast-furnaces (Table 28).

**152. Comparison of Blast- and Reverberatory-Furnace for Matting.**—The older discussions upon the relative merits of these two apparatus for smelting sulphide copper ores<sup>1</sup> have had to be revised to some extent to meet new conditions.<sup>2</sup> Many points have to be considered to arrive for a given locality at a

<sup>1</sup> Vivian, *Eng. Min. J.*, 1881, xxxi, 248.

Peters, *Min. Resources U. S.*, U. S. Geol. Surv., 1882, p. 270.

Howe, *Bull.* 26, U. S. Geol. Surv., 1885, p. 99.

Lang, *Eng. Min. J.*, 1890, l, 570.

<sup>2</sup> *Min. Sc. Press*, 1906, xcii, 136 (Editor), 138 (Neill), 197 (Mathewson), 215 (Bretherton) 279 (Hixon), 296 (Austin), 342 (Subscriber); 1907, xciv, 114 (Charles), 815 (Neill).

conclusion which is approximately correct; actual practice may be necessary to give a definitive answer. Some of the points are the following: The blast-furnace requires coarse ore; can make slags of high or low silicate degree, but requires generally much flux to obtain a slag of desired fluidity, and the large quantity of slag formed carries away much Cu although its assay-value is low; it eliminates impurities effectively, especially in pyritic work; uses a small amount of expensive coke; requires little labor but much power and cooling water; has small repairs; makes much dust; is cheap to build for a given tonnage; requires little space; locks up comparatively little capital. The reverberatory furnace, on the other hand, requires an extended roasting plant; is especially suited for fine ore (including the flue-dust of the blast-furnace); must make slags high in  $\text{SiO}_2$  and is therefore restricted to siliceous charges using little flux, and the higher slag-assays for Cu may be balanced by the small amount of slag made; it consumes enormous amounts of cheap coal (replaced sometimes by oil); the labor cost is high, the power consumption is low, especially if there are waste-heat boilers; the original cost, the floor space, and repair will always remain large, as will the capital locked up in the bath of matte and the sand-bottom. The metal locked up in the matte of a reverberatory furnace and a blast-furnace is about as 10 : 1.

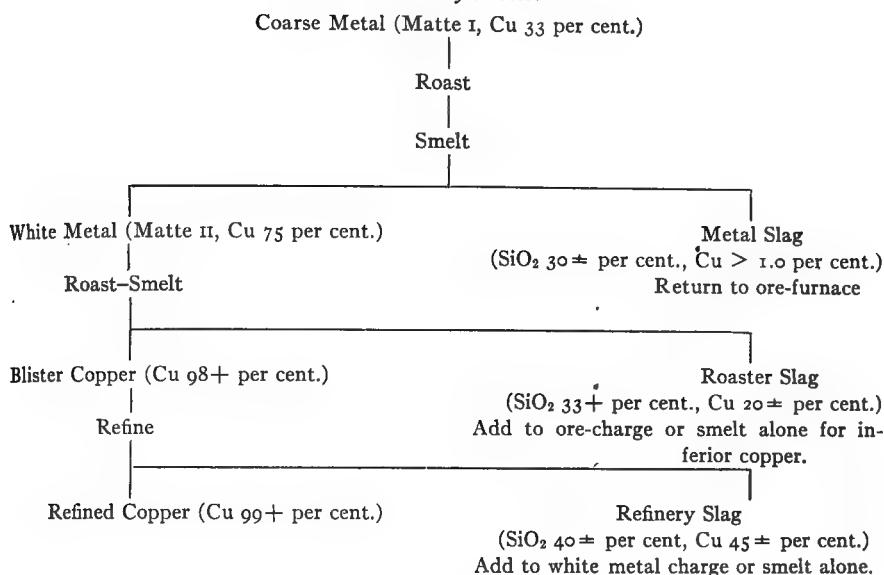
With most large plants both reverberatory and blast-furnaces are in successful operation, the former treating fine ore and flue-dust, and furnishing through its waste-heat boilers part of the power of the plant, the latter treating coarse ore.

**153. Production in the Reverberatory Furnace of Metallic Copper from Matte.**—Bringing the copper forward in the reverberatory furnace, from the first matte to the metallic state was the method employed in most American, English, and many European works; it has been superseded by converting, wherever this is permissible, but still holds its own in many places, at least for the production of metallic copper from matte containing Cu 70–80 per cent.

There were and probably still are in operation various ways of obtaining metallic copper in the reverberatory furnace from matte containing the old standard of Cu 33 per cent. (so-called *coarse metal*), characterized by a dark brown surface, a fracture bluish-black when hot and yellowish-brown to bronze when cold, granular to vesicular, and uneven. Two ways may serve as examples, the *Ordinary Process* with six steps, and the *Extra* or *Selecting Process* with seven steps; to these will be added the *Argo Process*, an adaptation of the selecting process to special ends.

**154. The Ordinary Process.**—The aim of this mode of operating is to bring forward the matte as quickly as possible. The result is that only a comparatively small proportion of impurity is eliminated and copper of ordinary grade produced. Hence it is suited mainly for ores which contain little As, Sb, Zn, Sn, Ni, Co, etc. The following tree gives an outline of the process:



*The Ordinary Process*

(1) ROASTING COARSE METAL.—The aim is to oxidize Fe that it may be slagged, S that it may be volatilized, and perhaps As and Sb that they may be eliminated. The roasting is carried far enough to oxidize all the S that is not needed in the subsequent smelting to combine with the Cu and some Fe to form white metal. If oxide copper ore is available for the smelting, the roasting can be cut short, as CuO will act upon undecomposed S-ide and drive off some S as SO<sub>2</sub>. Coarse- and fine-ore roasting kilns (§ 58 *et seq.*) are used occasionally when sulphurous gases are to be converted into H<sub>2</sub>SO<sub>4</sub>; the reverberatory furnace (§ 70 *et seq.*) is the common apparatus. Gibb<sup>1</sup> found that in roasting matte with Cu 33.40, As 0.185, Sb 0.060, Bi 0.017 per cent. there was eliminated As 35.4 per cent., Sb none, Bi 17.6 per cent. The expulsion of the impurities in matte is less marked than in ore on account of the smaller amount of S present.

(2) SMELTING ROASTED COARSE METAL FOR WHITE METAL.—The aim of the operation is to carry all the Cu into the matte and most of the Fe into the slag. Pure Cu<sub>2</sub>S (Cu 79.8 per cent.) cannot be made without forcing an excessive amount of Cu into the slag, hence white metal is allowed to retain from 4 to 8 per cent. Fe. The SiO<sub>2</sub> necessary for the slag comes in part from the sand adhering to the coarse metal (if tapped into sand molds), in part from the fettling of the furnace or from siliceous oxide ore; occasionally roaster- and refinery-slags are added to the charge, a practice to be avoided if feasible, as impurities are carried back into the process. The "metal furnace" has the same general form as the charge-fed ore-furnace. Table 61 gives a few old examples. As, in the United States at least, the first matte produced in the reverberatory furnace contains Cu from 40 to 50 per cent., and is brought forward by other means,

<sup>1</sup> *Tr. A. I. M. E.*, 1903, XXXIII, 658.

TABLE 61.—METAL FURNACES

Locality	Hearth	Grate	Charge, tons	Coal, lb. per charge	Charge, time of smelting, hr.	Reference
Mansfeld.....	13' 11' × 9' 10"	4' × 4'	6.5	3250	6	Leuschner, <i>Zt. Berg. Hütten. Salinen W. i. Pr.</i> , 1869, XVII, 135.
Oker.....	14' 1" × 9' 10"	3' 11" × 3' 3"	3	3300	8	Bräuning, <i>op. cit.</i> 1877, XXV, 133.
Cwm Avon.....	16' × 12'	4' × 4'	2	.....	12	Levy, <i>Rev. Univ. Min.</i> , 1884, XVI, 286.

this process in its old form<sup>1</sup> has little practical interest at present. In order to be economical, it would have to be worked in larger units. The chemical reactions taking place in smelting are similar to those in ore-smelting, excepting that the sulphurizing action by FeS must be more prominent than the reducing effect of Cu<sub>2</sub>S upon Cu<sub>2</sub>O or CuO, as there is very little ebullition, consequently little SO<sub>2</sub>. Thus Le Play<sup>1</sup> found that upon heating a charge of 3520 lb., first matte low in Cu trickled through the charge and collected on the hearth; in from 3 to 4 hr. three distinct layers could be distinguished; fluid matte on the bottom, next well-fused slag, and lastly partly fused charge. The last resolved itself into well-fused slag and matte. During the fusion the matte grew richer in Cu and the slag poorer as seen in Table 62.

TABLE 62. CHANGES OF COPPER-CONTENT IN MATTE AND SLAG

Time after charging	Matte, Cu, per cent.	Slag, Cu, per cent.
3 hr. 10 min.....	54	9
4 hr. 0 min.....	52	9
5 hr. 0 min.....	65	5
5 hr. 50 min.....	74	3.5

In charging the furnace, the coarse parts are first introduced and then covered with the fine, as these are more difficult of fusion and adhere more readily to the bottom than the coarse. About 1 hr. before the fusion is completed, the bottom is scraped to bring adhering parts to the surface. The slag is skimmed and the matte tapped, or both are tapped together into a series of overflow slag-pots.

White metal has a dark bluish to grayish color, is compact, brittle, more or less crystalline and free from moss copper. An analysis of high-grade white metal gave Le Play<sup>2</sup> Cu 77.4, Fe 0.7, Ni.Co.Mn trace, Sn.As 0.1, S 21.0, Insol. 0.3 per cent.; one of lower grade, Cu 64.8, Fe 0.9, Ni.Co.Mn 0.5, Sn.As 0.7, S 22.6, Insol. 1.8 per cent.; an average of fourteen samples, Cu 73.2 per cent. The slag contained, SiO<sub>2</sub> 31.0, FeO 56.0, Al<sub>2</sub>O<sub>3</sub> 6.9, CuO 3.5, MgO 0.6,

<sup>1</sup> *Op. cit.*, p. 423.<sup>2</sup> *Op. cit.*, p. 419.

Other Oxides 0.3, Entangled Matte 1.67 per cent. In smelting roasted coarse metal with Cu 31.04, As 0.111, Sb 0.062, Bi 0.013 per cent., Gibb<sup>1</sup> found the elimination to be As 58.5, Sb 59.0 and Bi 35.7 per cent.

3. ROAST-SMELTING OF WHITE METAL FOR BLISTER COPPER.—In this process, called in English technical literature "Roasting," the two operations of roasting and smelting are carried on in the same furnace, the smelting following immediately after roasting. The aim is to oxidize all the Fe and part of the Cu and S by melting cakes of white metal slowly in a strongly oxidizing atmosphere so that when the temperature is raised to liquefy the mushy bath of sulphide and oxide, the two will react upon one another and form Cu and SO<sub>2</sub>, while the FeO<sub>x</sub> will combine with SiO<sub>2</sub> and form a slag. The blister copper retains some impurities to be removed by subsequent fire-refining. The slag formed is very rich in Cu, and is retreated.

The "blister-furnace" resembles in its general form the metal furnace; special attention, however, is given for air to have free access to the charge during the first stage of the process. The fire-bridge is made hollow and has air-ports extending into the hearth, so that air enters through the bridge, and through the side doors; sometimes openings are provided near the ends of the fire-bridge for the admission of air; air may be blown through pipes inserted into these side openings. The furnace has to be strongly built, as the hearth holds a heavy charge. Table 63 gives a few examples of older furnaces.<sup>2</sup>

TABLE 63.—BLISTER-FURNACES

Locality	Hearth	Fire-box	Charge, tons	Time, hr.	Coal, lb. per ton charge	Reference
Wales.....			4.08	24	1190	Le Play, <i>loc. cit.</i>
Cwm Avon.....	16' × 12'	4' × 4'	5	24	.....	Levy, <i>loc. cit.</i>
Caldera.....	16' 6" × 11' 6"	5' 8" × 5' 3"	6.3	24	1600	Howe, <i>loc. cit.</i>
U. S.....			25	.....	.....	Private notes.

The process consists of five operations:

(a) Cakes of white metal are charged with paddles through the side doors, piled up almost to the roof in such a manner as to leave open channels between the cakes, and passages for air and gases along the sides and between matte and roof; a space of about 4 ft. is left uncovered between fire-bridge and charge.

(b) The doors are closed, and the fire is urged for about  $\frac{1}{2}$  hr. until the cakes just begin to melt; then the doors are more or less opened, and the temperature of the furnace is held at this or a slightly more elevated temperature in order to fuse the matte slowly. The parts of matte fusing first will trickle down over the still unfused parts, and both will be oxidized in the strongly oxidizing atmosphere. In about half the time given to the whole treatment, the charge will have been converted into a half-fused mushy mass that has been hardened somewhat

<sup>1</sup> *Tr. A. I. M. E.*, 1903, XXXIII, 660.

<sup>2</sup> Drawings of gas-fired blister-furnace with regenerative chambers are given in Peters "Modern Copper Smelting," 1895, p. 509.

near the doors by the inrushing air; the reaction between  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{O}$  will have been started causing Cu to be set free, the latter collecting on the bottom, the  $\text{SO}_2$  passing off with a hissing noise.

(c) The air-ports and side doors are closed and the fire is urged to liquefy the charge completely; the liberations of Cu and  $\text{SO}_2$  continue, oxidized Fe rises to the surface, enters the slag, and is skimmed. There remains in the furnace a bath of Cu covered with a thin layer of matte.

(d) Air-ports and fire-door are opened to cool the metal and oxidize the matte. With much matte, rabbling and skimming become necessary to oxidize the sulphide and remove the oxide formed. Cooling is continued until the Cu begins to harden, in order to finish the action of  $\text{Cu}_2\text{S}$  upon  $\text{Cu}_2\text{O}$ , and to assist the expulsion of  $\text{SO}_2$  held in solution by the fluid copper. The  $\text{SO}_2$  in passing off through the half-fluid Cu forms crater-like excrescences and causes the metal to swell to from two to three times its original volume; the spongy mass becomes more or less oxidized by being exposed to air at this temperature.<sup>1</sup>

(e) The temperature is now raised again with the air-ports in the fire-bridge, kept open, and the Cu is completely liquefied; the slag floating on top is skimmed the blister copper tapped and collected in sand or cast-iron molds. The runners connecting the cakes of Cu in the molds are broken while hot.

Blister copper receives its name from the cavities in the body and the excrescences on the surface caused by dissolved  $\text{SO}_2$  being given off while the metal is solidifying. Its surface is dark from oxidation, the fracture brick to dark red and granular to fibrous; the blisters vary in color from brown to yellow. Table 64 gives the chemical composition of blister copper.

TABLE 64.—BLISTER COPPER

Locality	Cu	Fe	Ni, Co, Mn	Zn	Sn, Sb	Sn, As	S	Reference
Kaafjord. . . .	99.2-99.4	0.1-0.2	0.2-0.3	0-0.02	.....	.....	0.1-0.12	Kerl, "Metallnüttenkunde," p. 215.
Swansea. . . . .	98.4	0.7	0.3	.....	.....	0.4	0.2	
Swansea. . . . .	97.5	0.7	.....	.....	1.0	.....	0.2	Le Play, <i>op. cit.</i> , p. 486.
Swansea. . . . .	98.0	0.5	.....	.....	0.7	.....	0.3	
Swansea. . . . .	98.5	0.8	.....	.....	.....	.....	0.1	

The composition of roaster-slag (average Cu 20 per cent.) is given in Table 65.

TABLE 65.—ROASTER-SLAG

Locality	$\text{SiO}_2$	$\text{FeO}$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{Ca}_2\text{O}$	Cu	Ni, Co, Mn	$\text{SnO}$	$\text{ZnO}$	S	Reference
Wales. . . . .	47.5	28.0	3.0	tr.	tr.	16.9	2.0	0.9	0.3	2.0	..	Le Play, p. 487.
Kaafjord. . .	36.0	7.0	6.0	2.7	0.8	43.2	.....	4.9	0.6	3.2	..	
Wales. . . . .	45.0	28.0	.....	.....	.....	25.0	.....	.....	.....	.....	2	Percy, p. 363.

<sup>1</sup> Vivian, *Eng. Min. J.*, 1881, XXXI, 250.

The elimination of impurities by volatilization as shown by Gibb<sup>1</sup> is As 18, Sb 20.5, Bi 73.4 per cent. His comparison of roast-smelting and converting.<sup>2</sup> is given in § 168. The research of Keller<sup>3</sup> has shown that for every one part of Cu there may be slagged 1.95 Pb, 0.80 Bi, 2.02 Sb, 0.38 As, and 0.98 Se-Te. The losses in precious metal are said to be very low. This is given in Europe as one of the reasons for the preference given to roast-smelting over converting for bringing forward matte with Cu 80 per cent. to the metallic state, as in the latter process (§ 170), the blister-forming stage is known to be accompanied by considerable losses.

4. THE DIRECT (REACTOR, NICHOLS-JAMES) PROCESS.<sup>4</sup>—This is a modification of roast-smelting in which coarsely crushed raw and roasted white metal are mixed, the correct proportions (usually 1:2) being ascertained by crucible experiment, and melted down in the reverberatory furnace where the same products will be formed as in roast-smelting. This process is in operation at Mansfeld, Germany, where according to Stahl,<sup>5</sup> in treating 111,757 tons of matte and oxides of copper, with Cu 74.46 per cent. and Ag 65 oz. per ton, the loss by volatilization in Cu was only 1.303 per cent. and in Ag 2.5091 per cent.

In smelting sulphide copper ore by the ordinary process as outlined, including the refining of blister copper, the total elimination of impurities was found by Keller<sup>6</sup> to be Pb 99, Se-Te, 60, Bi 54, Sb 50 and As 21 per cent.

5. REFINING OF BLISTER COPPER.—This will be taken up in § 186.

**155. The Extra or Selecting Process.**<sup>7</sup>—The aim of the process is to produce from sulphide ore the highest grade—"Best Selected" or "B. S."—copper. This is accomplished by two means:

(1) By bringing forward the copper more slowly than in the ordinary process, whereby impurities, such as As and Sb, remaining longer in the state of sulphide, are more easily eliminated, and,

(2) By forming "bottoms," *i.e.*, roast-smelting in such a manner as to produce some metallic Cu which carries down with it most of the remaining impuri-

<sup>1</sup> *Tr. A. I. M. E.*, 1903, XXIII, 662.

<sup>2</sup> *Tr. A. I. M. E.*, 1904, XXXIV, 957.

<sup>3</sup> *Tr. A. I. M. E.*, 1898, XXVIII, 127, 816; *Min. Ind.*, 1898, VII, 245, 1900, IX, 240.

<sup>4</sup> Vautin, *Tr. Inst. Min. Met.*, 1893-94, II, 76.

Peters, *Min. Ind.*, 1893, II, 269, "Modern Copper Smelting," 1895, p. 519.

Terrill, *Eng. Min. J.*, 1898, LXVI, 665.

Keller, *Min. Ind.*, 1898, VII, 244, 245; *Tr. A. I. M. E.*, 1898, XXVIII, 821.

Kroupa, *Berg. Hüttenm. Z.*, 1899, LVIII, 483; *Oest. Zt. Berg. Hüttenw.*, 1899, XLVII,

241, 395.

Thofern-Seine, *Eng. Min. J.*, 1902, LXXIV, 340.

Glenn, *op. cit.*, 1902, LXXIV, 381.

Wagner-Primrose, *op. cit.*, 1907, LXXXIV, 671.

Stahl, *Metallurgie*, 1908, V, 353.

Styri, *op. cit.*, 1912, IX, 426, 449.

<sup>5</sup> *Metallurgie*, 1908, V, 353.

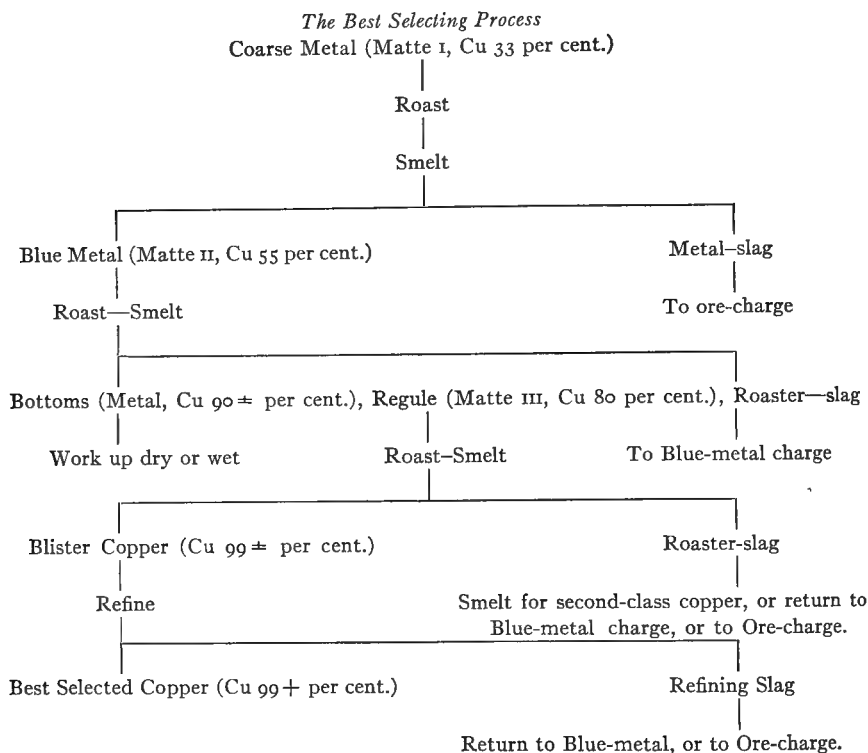
<sup>6</sup> *Tr. A. I. M. E.*, 1898, XXVIII, 145.

<sup>7</sup> Gibb, *3d Report, Alloys Research Committee*, 1895, pp. 254-286.

Peters, *Eng. Min. J.*, 1895, XLIX, 512.

Keller, *Min. Ind.*, 1900, IX, 512.

ties and thereby purifies the remaining rich matte (Cu, 80 per cent.) called "regule." Bottoms are refined in the same way as is blister copper, giving an inferior brand of copper, or are worked up in the wet way. The matte is treated as is the white metal in the ordinary process and furnishes a very pure copper. If impure ores are treated by this process, there will result "G. O. B." (good ordinary brand) or "G. M. B." (good merchant brand) copper which is the "Standard" brand<sup>1</sup> of the London Metal Exchange. The accompanying tree gives an outline of the operations.



In roasting coarse metal for the subsequent production of blue metal, either the elimination of S is not carried so far as would be necessary in smelting for white metal, or, as is more common, no change is made in the roasting, but unroasted rich sulphide ore is added to the smelting charge. Roast-smelting of coarse for blue metal has become obsolete. The smelting furnace for producing blister copper has the form and size of the white-metal furnace. A furnace used in the *ordinary process* may not be employed for the *selecting process*, as the working bottom may take up some impurity and become "poisoned"; for the same reason a furnace for *extra process* may not be used occasionally for an operation in the *ordinary process*. The management of the furnace is the same as in smelting for white metal.

<sup>1</sup> *Eng. Min. J.*, 1909, LXXXVII, 375.

"Blue Metal" has a purplish-blue color; the fracture when cold is purplish-red, uneven, and has a submetallic luster; the matte is brittle and contains moss copper. An analysis by Le Play<sup>1</sup> gives Cu 56.7, Fe 16.3, Ni 1.6, Mn trace, Sn 1.2, As trace, S 23.0, Insol. 0.5 per cent. The blue-metal slag has no particular characteristics. Le Play's analysis<sup>2</sup> gives SiO<sub>2</sub> 36.0, Cu<sub>2</sub>O 0.7, FeO 54.4, Al<sub>2</sub>O<sub>3</sub> 0.8, MgO 0.2, CaO 1.2, Other Oxides 2.5, Matte 4.2 (= Cu 2.4, Fe 0.8, S 1.0) per cent. Matte lying between coarse metal (Cu 33 per cent.) and blue metal (Cu 55 per cent.) has been called "red metal."

In roast-smelting for bottom and regule the aim during the roasting period is to drive off enough S so that in the fusion all the Fe may enter the slag and enough metallic Cu be produced to carry down with it all the remaining impurities in order that resulting 80-per cent. matte (regule, spongy regulus) shall be as pure as it can be made. The investigations of Gibb<sup>3</sup> have shown that the amount of copper separated as bottom should not exceed 20 per cent. of the Cu-content of the charge, the usual amount being 14 per cent., as a larger percentage not only diminishes the direct yield in Cu, but may also impair its purity. Table 66 gives some of the results of Gibb's work.

TABLE 66.—ELIMINATION OF IMPURITIES FROM MATTE BY BOTTOMS

Impurity	Per cent. of Cu-content of matte separating as bottom	Per cent. of impurity of matte entering the bottom	Impurity	Per cent. of Cu-content of matte separating as bottom	Per cent. of impurity of matte entering the bottom
Sn.....	20.6	93.4	As.....	25.2	60.2
Sb.....	8.2	21.0	Ni.....	8.0	8.2 <sup>6</sup>
Sb.....	17.3	80.8	Ni+As....	19.3	47.9 Ni+77.7 As
Sb.....	47.5	93.7	Ni+As....	28.3	? +83.9 As
Sb.....	54.5	92.6 <sup>4</sup>	Ni+As, Ag.....		Ag diminished by Ni+As.
Bi.....	8.2	11.1	Au.....	8.2	41.5
Bi.....	16.0	43.1 <sup>5</sup>	Au.....	14.4	100.0
Bi.....	47.5	47.6	Ag.....	19.0	42.9 <sup>7</sup>
As.....	8.2	21.5	Ag, Pb, Sb, Au.....	35(+Fe)	74.5 Ag, 83.5 Pb, 97.0 Sb, 92.8 Au
As.....	16.0	30.6	.....		.....

The furnace, the mode of operating, and the chemical reactions taking place are similar to those in roast-smelting white metal. Analyses of products (bottom, regule and slag), are given in Table 67.

**156. The Argo Process.**<sup>8</sup>—The characteristics of this process are that the

<sup>1</sup> *Op. cit.*, p. 439.

<sup>2</sup> *Op. cit.*, p. 440.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> Decrease.

<sup>5</sup> Practical maximum.

<sup>6</sup> Practically no concentration.

<sup>7</sup> Maximum.

<sup>8</sup> Egleston, *Tr. A. I. M. E.*, 1875-76, IV, 276 (Black Hawk).

Pearce, R., *op. cit.*, 1889-90, XVIII, 55 (Argo).

Peters, *Eng. Min. J.*, 1890, L, 189.

Ulke, *Min. Ind.*, 1893, II, 290.

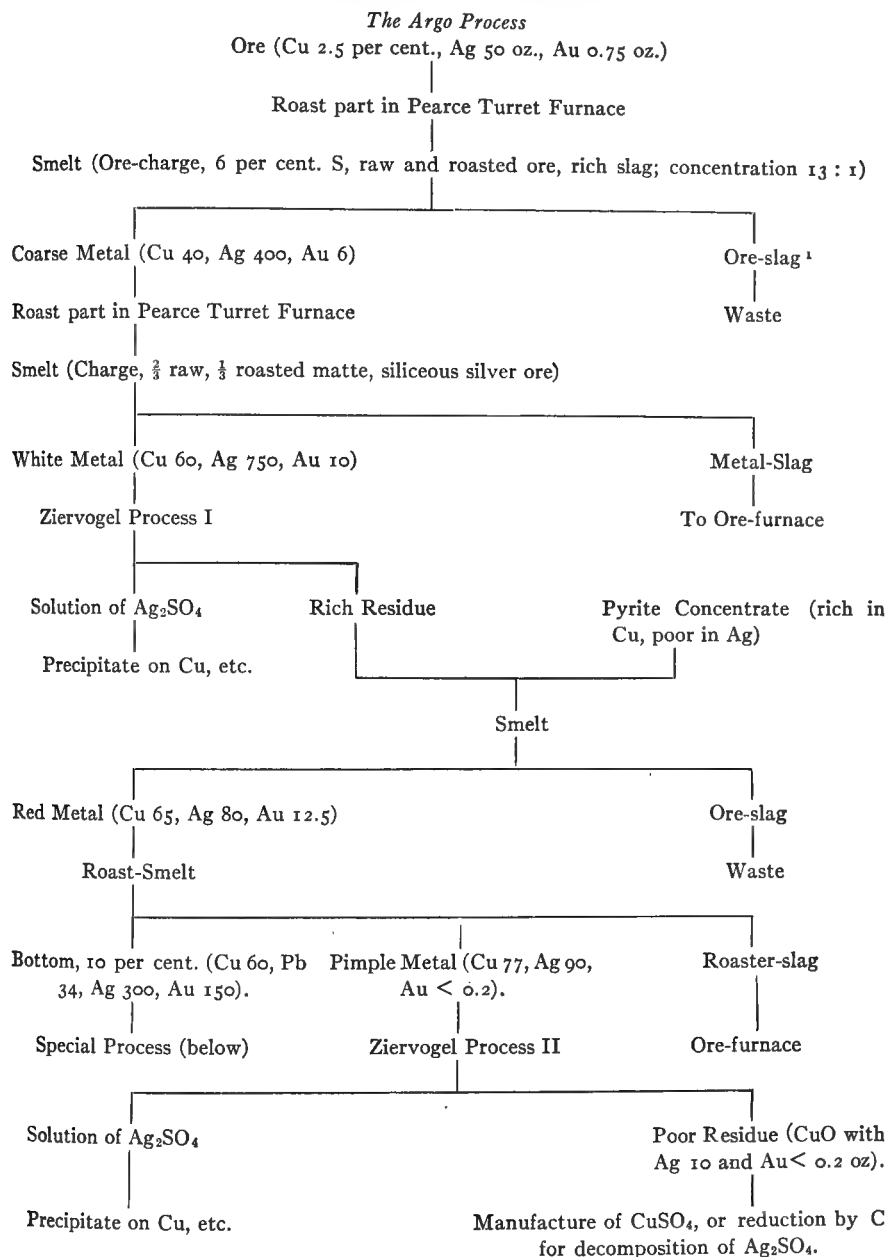
TABLE 67.—ANALYSES OF PRODUCTS FROM ROAST-SMELTING BLUE METAL (RED METAL)

Product, locality	Cu, per cent.	Fe, per cent.	S, per cent.	As, per cent.	NiCo, per cent.	Pb, per cent.	Zn, per cent.	Sb, per cent.	Bi, per cent.	Sn, per cent.	FeNi, Co, per cent.	In- sol., per cent.	Ag, oz. per ton	Au, oz. per ton	Reference
Bottom, Wales...	74.0	2.5	3.9			0.8		4.5		13.8					Percy, <i>op. cit.</i> , p. 366.
Bottom, Wales...	86.5 <sup>1</sup>		6.9	1.8						0.7	3.2				Le Play, <i>op. cit.</i> , p. 453.
Bottom, Wales...	92.5 <sup>2</sup>		4.8	0.4						0.2	1.6				Le Play, <i>op. cit.</i> , p. 474.
Bottom, Argo...	60.04	0.08	1.68	0.44		33.61	0.15		0.40				393	157	Pearce, <i>Tr. A. I. M. E.</i> , 1889-90, xviii, 69.
Bottom, England.	83-87	0.5	1-3	5-7		3-5						0.5			Gilchrist, <i>J. Soc. Chem.</i> <i>Ind.</i> , 1891, x, 4.
Regule, Wales...	77.5	2.2	20.1	tr.	tr.										Le Play, <i>op. cit.</i> , p. 467.
Regule, Wales...	81.1 <sup>3</sup>	0.2	18.5										90		Le Play, <i>op. cit.</i> , p. 473.
Regule, Argo...	77.0														Pearce, <i>Tr. A. I. M. E.</i> , 1889-90, xviii, 69.
Regule, Argo...					Cu <sub>2</sub> O and Cu <sub>2</sub> S										
Slag, Wales...	SiO <sub>2</sub>	FeO	Al <sub>2</sub> O <sub>3</sub>	CaO	12.0										Le Play, <i>op. cit.</i> , p. 473
	34	5.2	1.0	1.0											

<sup>1</sup> From red metal. <sup>2</sup> From regule. <sup>3</sup> Contains metallic Cu, made from red metal (Cu 62 per cent.)



Welsh selecting process has been adapted to the collection of Ag and Au in copper matte from which the Au is recovered by the production of bottoms treated by a fire process, and the Ag extracted by the Ziervogel process (§ 237). The accompanying tree gives the leading features of the mode of operating.



<sup>1</sup>  $\text{SiO}_2$  33.9,  $\text{FeO}$  13.9,  $\text{BaSO}_4$  15.5,  $\text{Al}_2\text{O}_3$  5.6,  $\text{CaO}$  4.8,  $\text{MgO}$  2.7,  $\text{ZnO}$  6.1,  $\text{Cu}$  3.0,  $\text{S}$  5.1 (Peters, "Principles," p. 188); other examples Pearce, *op. cit.*, p. 63.

The roasting and smelting operations have already been discussed. The Ziervogel process will be outlined in § 237. There remains the Pearce process.

THE PEARCE GOLD SEPARATING PROCESS,<sup>1</sup> which was carried on in secret from the starting of the works of the Boston & Colorado Smelting Co. at Black Hawk, Colo., in 1874 until the closing of the Argo, Colo., plant in 1909,<sup>2</sup> is based upon the strong affinity<sup>3</sup> S has for Cu in comparison with Au, Ag and other metals found in copper bottoms. If a granulated bottom is repeatedly fused with pyrite in right proportions, Cu, Ag, and the other metals will be "stripped," *i.e.*, taken up by the matte that is formed, while impure Au will remain behind to be purified by niter fusions. The same principle of working has been developed independently by Roessler<sup>4</sup> for the refining of base jeweller bars. At Argo the practice was as follows:

A charge of 6400 lb. bottom (0.4–0.5 per cent. Au) is purified by melting in 8 hr. on the brick hearth of a reverberatory furnace in an oxidizing atmosphere, the temperature being raised toward the end with doors and ports in fire-bridge closed to render the whole thoroughly fluid; the fluid charge is rabbled, the slag skimmed, and the alloy tapped at the side, conveyed through a cast-iron launder into a tank of cold water; the stream of metal falling first on to a spruce pole to spray it before it strikes water. The granules, weighing about 4400 lb., are caught in a perforated pan, removed, and dried. From 14 to 16 charges of bottom furnish enough material for from 22 to 30 charges for the first stripping. A mixture of 2200 lb. granules and 1500 pyrite is melted in a smaller reverberatory furnace; the slag is skimmed, and matte together with alloy tapped into communicating sand molds; the alloy weighs from 625 to 650 lb. When enough alloy has been accumulated, it is melted in a reverberatory furnace as was the crude bottom, skimmed, tapped, and granulated; the granules contain from 2 to 3 per cent. Au. The first stripping is followed by a second, giving an alloy with 25 per cent. Au, and this by a third which concentrates the Au to 45 per cent. The further refining is carried on in graphite crucibles; three strippings bring the Au to 900 fineness, when a final treatment with niter in clay crucibles removes more base metal and furnishes a gold bar of about 957 fineness. The mattes which are gold-bearing are returned to preceding operations as are other intermediary products.

#### IV. SMELTING IN THE CONVERTER

##### 157. Converting Copper Matte in General.<sup>5</sup>—In the converting process,

<sup>1</sup> H. V. Pearce, *Tr. A. I. M. E.*, 1908, XXXIX, 722.

<sup>2</sup> *Eng. Min. J.*, 1909, LXXXVII, 787.

<sup>3</sup> Hofman, "General Metallurgy," 1913, p. 74.

<sup>4</sup> *Berg. Hüttenm. Z.*, 1882, XLI, 152; *Eng. Min. J.*, 1882, XXXIII, 261.

<sup>5</sup> Douglas, *Tr. Inst. Min. and Met.*, 1899–1900, XIII, 2.

Jannetaz, P. "Les Convertisseurs pour Cuivre," Baudry, Paris, 1902.

Kroupa, *Oest. Zt. Berg. Hüttenw.*, 1903, LI, 695, 715.

Mayr, F. "Das Bessemern von Kupfersteinen," Craz und Gerlach, Freiberg, 1906.

Sticht, R. C. "Progress in Rapid Oxidation Processes Applied to Copper Smelting," Australian Assoc. Adv. Sciences, Jan., 1907.

air in thin streams is forced through Cu-Fe matte held in a refractory vessel at 1150–1200° C.; Fe is oxidized to FeO and combines with SiO<sub>2</sub> forming a slag; S forms SO<sub>2</sub> and passes off; and Cu is set free to be cast into suitable forms; the oxidation of Fe and S, and the union of FeO and SiO<sub>2</sub> furnish the necessary heat.

The first attempt at enriching matte by a pneumatic process was that of A. Rath in 1866<sup>1</sup> who at Ducktown, Tenn., forced air through matter to oxidize Fe and S, and continued the process until 1875. In 1867 Semenikow of the Bogoslawsk mines, Ural Mts., proposed making blister copper in a converter; the working tests were carried out by Jossa and Laletin who published their results in the Russian Mining Magazine of May, 1870.<sup>2</sup> They succeeded in bringing forward coarse metal (Cu 31 per cent.) to white metal Cu 72–80 per cent.), but failed to produce blister copper.

Converting lay practically dormant until Manhès and David in 1880 at Egulles, France, succeeded in obtaining blister copper.<sup>3</sup> In 1883–84 their process was introduced at the works of the Parrot Silver & Copper Co. of Butte, Mont.<sup>4</sup> The original mode of procedure, of blowing in two separate stages, melting matte with Cu 35 per cent. and blowing to 80 per cent., followed by casting and remelting the white metal and blowing to blister copper, was retained until 1885<sup>5</sup> when A. J. Schumacher laid the foundation of the modern practice of starting with matte of 40–50 per cent. Cu and blowing to blister copper in two consecutive stages without any remelting of white metal. The last improvement was the working of direct matte instead of cupola matte, the matte being tapped from the blast-furnace settler or the reverberatory hearth either into a ladle and poured into the converter, or made to flow direct into it (now abandoned). This method was planned in 1890–91 by C. O. Parsons for Great Falls, Mont., and carried out there in 1892 by F. Klepetko.<sup>6</sup>

Modern American (acid) practice then represents the combined improvements of Schumacher and Parsons upon the original Manhès-David process.<sup>7</sup> So far the converter had always been lined with siliceous material which furnishes the SiO<sub>2</sub> necessary to slag the FeO. About 1888 Claude Vautin experimented with a basic lining at Cobar, Australia, but gave up the attempt. In 1890 Keller<sup>8</sup> made unsuccessful attempts at the Parrott smelter in Butte at

Hixon, H. W., "Notes on Lead and Copper Smelting," McGraw-Hill Book Co., New York, 1908.

Peters, E. D., "Principles of Copper Smelting," "Practice of Copper Smelting," McGraw-Hill Book Co., 1907 and 1911.

<sup>1</sup> U. S. Patent No. 57376, Aug. 21, 1866; *Eng. Min. J.*, 1879, XXVII, 260, 1883, XXXV, 250.

<sup>2</sup> *Berg. Hüttenm. Z.*, 1871, XXX, 7, 17, 57.

<sup>3</sup> Grüner, *Bull. soc. d'Encouragement*, 1882, IX, 439; *Ann. Mines*, 1883, III, 429; *Bull. Soc. Ind. Min.*, 1885, XIV, 607.

<sup>4</sup> Repath, *Min. Sc. Press*, 1902, LXXXV, 144.

<sup>5</sup> Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 261.

<sup>6</sup> Hofman, *loc. cit.*

<sup>7</sup> See also Hass: "Development of Converter Practice," *Min. Sc. Press*, 1913, CVII, 653.

<sup>8</sup> Peters, "Modern Copper Smelting," 1895, p. 510.

Mathewson, *Tr. A. I. M. E.*, 1913, XLVI, 469.

Keller, *Tr. A. I. M. E.*, 1913, XLVI, 474.

converting matte in a vessel lined with magnesite. Others did the same at the old Anaconda and the Boston and Montana works. Later Westinghouse<sup>1</sup> experimented first at Pittsburg, Pa., and later at Ely, Vt., with a basic lining for pyritic smelting; Baggaley<sup>2</sup> worked in 1903 along similar lines and with converting at the Pittsmont smelter, Butte, Mont., but did not succeed entirely with his ideas. The work at the plant of the U. S. Smelting Co. at Midvale, Utah, met with a similar result.

The first successful converting in a vessel lined with basic, or rather neutral material, is that of Pearce and Smith in 1909, at Baltimore.<sup>3</sup> The pneumatic treatment of matte in a converter with a neutral lining, the  $\text{SiO}_2$  necessary being furnished by the addition of warmed acid ore, has so many advantages over the original acid process that it has largely replaced the latter.

In a discussion of converting, it is convenient, for the present at least, to keep separate the acid and basic converters. With each there will have to be considered (1) the apparatus, *i.e.*, the converter with its manipulation and lining, the blast, and the arrangement of plant; (2) the chemistry and mode of operating, the elimination of impurities, and the thermal features; and (3) the products and their disposal, the loss, and the cost.

#### a. Converting in Vessel with Acid Lining

**158. The Converter.**<sup>4</sup>—Matte converters have this in common, that they are side blown and not bottom blown as is the case with all large steel converters. They are usually classed as *Upright* and *Horizontal*.

**159. The Upright (Manhès) Converter.**<sup>5</sup>—In his first attempt at converting, Manhès used a pear-shaped bottom-blown upright vessel with a capacity of 440 lb. matte. At the beginning of a blow everything went smoothly; toward the end the slag thickened from having been overblown and was ejected in part; metallic copper solidified, having been cooled by air passing through it, and choked the vertical tuyère openings in the bottom. He therefore placed the tuyères in the side a short distance above the bottom lining, and thereby furnished a space beneath them in which the metallic copper formed would be out of reach of the blast, could settle, and be poured off later with the slag.<sup>6</sup>

<sup>1</sup> *Metallurgie*, 1904, I, 346.

<sup>2</sup> Heywood, *Eng. Min. J.*, 1906, LXXXI, 574; *Min. Sc. Press*, 1906, XCII, 281.

Baggaley, *Bull.* 83, *A. I. M. E.*, Nov., 1913, p. 2677.

<sup>3</sup> U. S. Patents, Nos. 942346 and 942661, Dec. 7, 1909; Nos. 942973 and 943280, Dec. 14, 1909; Vail, *Eng. Min. J.*, 1910, LXXXIX, 563; Editor, *op. cit.*, 1914, XCVII, 720.

<sup>4</sup> Christensen, *Min. World*, 1910, XXXIII, 1036.

<sup>5</sup> Wheeler-Krejci, *Tr. A. I. M. E.*, 1913, XLVI.

<sup>6</sup> Experiments at Great Falls, Mont. (Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 304; Wheeler-Krejci, *loc. cit.*) with an upright converter (13 ft. high and 9 ft. in diam., an initial charge of 50 tons of 50-per-cent. matte) were satisfactory as far as the bringing forward to blister copper was concerned which remained sufficiently fluid to permit pouring; they were not followed up, as the life of the bottom was too short. The difference in the two cases is due to the small amount of charge treated by Manhès which was chilled, and to the fact that his slag was not skimmed and hence was overblown, causing some  $\text{FeO}$  to be changed into  $\text{Fe}_3\text{O}_4$ , infusible at converter temperature.

The leading data of the original converter of Eguilles are given in Table 68. The original Parrot converter of 1894<sup>1</sup> was a copy of that of Eguilles; its general form and the details of construction were changed to meet the new conditions. Dimensions and working results are given in Table 68. The old Anaconda converter<sup>2</sup> and the plant are described by Hixon.<sup>3</sup>

The Stallmann converter of 1890, square in plan and curved in such a way as to reduce the blowing-out of molten material, was in operation at Anaconda for four years, but was then replaced by the circular type. It is still doing good service at Mount Lyell, Tasmania, where it was introduced about 1897.<sup>4</sup>

The two leading upright converters to-day are those at Aguas Calientes, Mexico,<sup>5</sup> shown in front elevation in Fig. 321, and at Great Falls, Mont., built in 1892. Figs. 322-324 give the details of the converter of 1904.

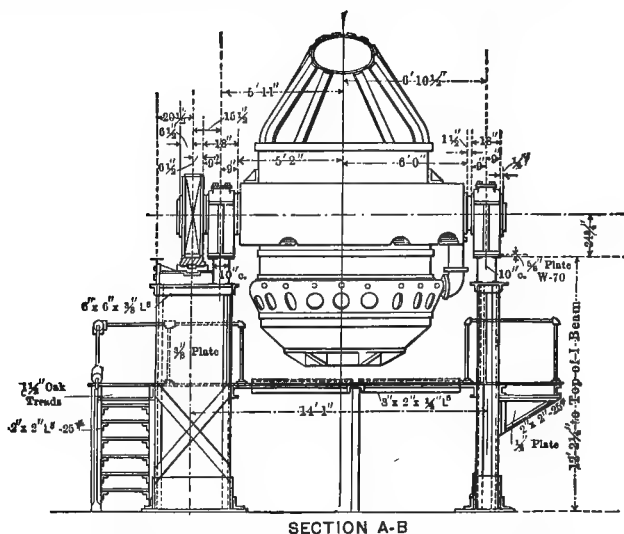


FIG. 321.—Upright converter of Aguas Calientes.

To the left of Fig. 321 are seen the horizontal rack and the pinion by means of which the converter is rotated in a vertical plane. The details of the converter of 1911 are given in Table 68.

The Great Falls converter of 1904, which is similar to the Aguas Calientes type consists of an upright cylindrical boiler-iron shell, *A*, with refractory lining, *b*, supported from a cast-iron trunnion-ring, *c*, by a pair of trunnions, *d*, in such a way as to permit swinging in a vertical plane for the reception of matte and

<sup>1</sup> Peters, "Modern Copper Smelting," 1895, p. 529.

<sup>2</sup> Stickney, *Eng. Min. J.*, 1893, LV, 370; 392, 417; *Min. Ind.*, 1892, I, 151.

<sup>8</sup> "Notes on Copper and Lead Smelting," 1908, p. 95.

<sup>4</sup> Peters, "Modern Copper Smelting," 1895, p. 530.

Faws, *Tr. Inst. Min. and Met.*, 1895-96, IV, 279.

Sticht, Presidential Address, p. 33.

<sup>6</sup> Hamilton, *Bull.* 83, *A. I. M. E.*, Nov., 1913, p. 2672.

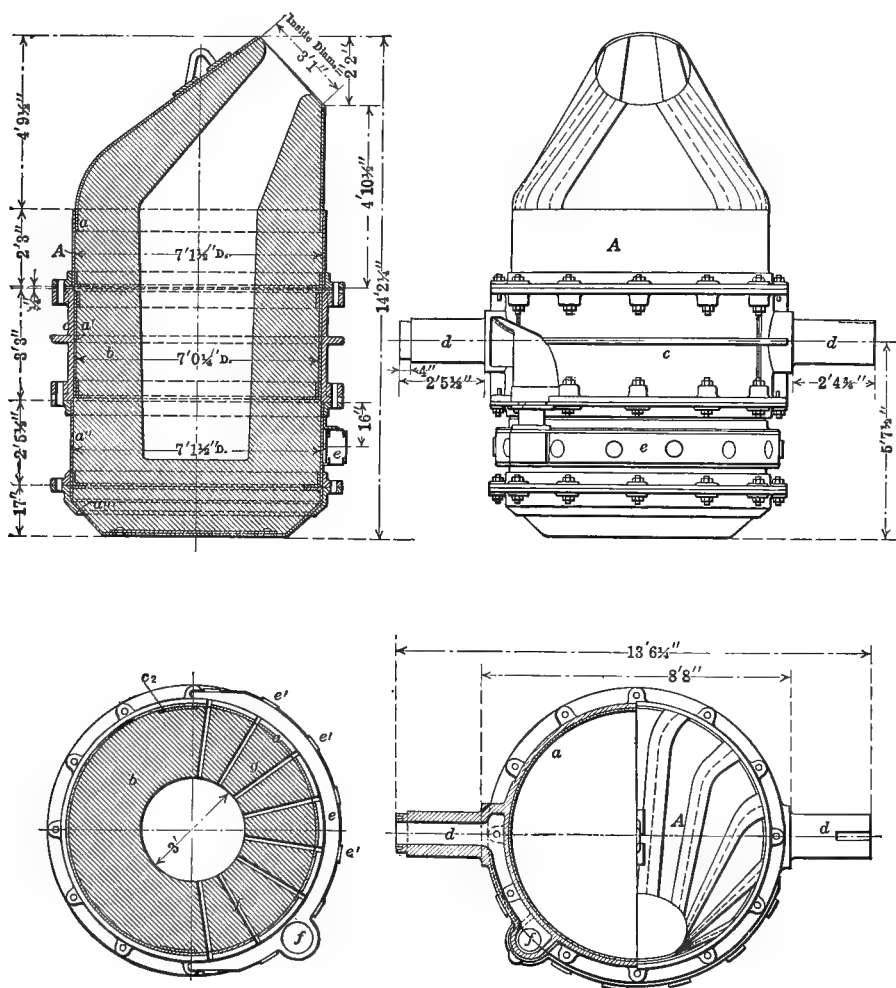
TABLE 68.—ACID

	Upright					
	Manhès, Eguilles, 1880	Parrot Copper and Silver Min. Co.	Boston & Montana, Great Falls			Agua Calientes
Cylinder, height outside.....	7' 6"	8' 6"	8' 9"	12'	12'	16'
Cylinder, diameter outside.....	4' 8"	5'	front-back 9'9,"width trunnion 8' 9"	front-back 10,' width trunnion 10'	12'	8' 1½"
Bottom, height outside.....			7' 8"	7' 8"	7' 8"	
Throat, diameter.....	¾'	2' 5"	3' 4½"	3' 4½"	3' 4½"	3'
Shell cylinder, thickness.....		1½"	½"	½"	½"	½"
Shell head, thickness.....		½"	½"	½"	½"	½"
Lining, character.....	Quartz & clay	Quartz & clay	Ore	Ore	Ore	Siliceous ore & clay
Lining, thickness at bottom.....	12"	18"	33"	30"	30"	23"
Lining, thickness at tuyères.....	10"	18"	39"	55"	65"	31½"
Lining, thickness opposite tuyères....	10"	18"	25"	22"	16"	31½"
Lining, thickness at hood, tuyère side	5½"	12"	27"	37"	37"	21"
Lining, thickness at hood, opposite tuy- ère side.	5½"	12"	34"	38"	38"	21"
Tuyères, number of.....	18	16"	12	15	15	12
Tuyères, diameter.....	0.5" & 0.6"	¾"	1"	1"	1"	2"
Tuyères, height above bottom lining..	6"	6"	2½"	5½"	5½"	7"
Charge, first, lb.....	2,000	2,500	6,500	8,500	8,500	5,000 -11,000
Charge, last before repairing, lb.....		9,000	11,500	18,500	18,500	33,000 -66,000
Blow, duration, min.....	25-30	80	170	170	170	90-125
Blows, number in 24 hr.....	16	14	7	7	7	4
Blast, pressure, lb. per sq. in.....	12-20	11	16	16	16	13½-13½
Grade of matte blown, per cent. Cu..	33	45	40-50	40-50	40-50	38-42
Charges, number per lining.....	7-8	9	5	6	6	11
Tons copper per lining.....		8	22	36	40	13.5
Men, per shift.....			Converting 2, accessory	Converting 2, accessory	Converting 2, accessory	18
Number of stands.....	6	3	2½ 12	2½ 12	2½ 12	
Number of shells.....		7				

## CONVERTERS

Horizontal								
Manhès-David, Jeres Lanteira	Copper Queen	Balaklala Con. Copper Co.	Tennessee Copper Co.	Shannon Copper Co.	Granby Con. Min. Smelt. Power Co.	Mammoth Copper Min. Co.	British Columbia Copper Co.	Anaconda Copper Min. Co.
4' 3" 4' 2"	8' 5' 8"	8' 4" 8'	10' 6" 7'	10' 6" 7' 6"	10' 6" 7'	7' 3" 8'	10' 6" 7'	12' 6" 8'
1' 10" 1"	2' 18"	4' 1 1/2" plate	3' 7" 1 1/2"	2' 6" 1 1/2"	4' 1 1/2"	3' 10" 1 1/2"	2' 10" 1 1/2"	3' 9" 1 1/2"
1"	1 1/2"	1 1/2" cast	1"	1-3" cast	1 1/2"	1 & 1 1/2" cast	1 1/2"	1 1/2"
Quartz & clay	Quartz & clay	Brick, 1 clay: 5-7 quartz; lining 2 clay: 3 quartz	Fire-brick and siliceous copper ore	2 siliceous ore: 1 fine concentrates	Siliceous gold-copper ore	Siliceous ore	7 siliceous gold ore (80% SiO <sub>2</sub> ): 1 clay	Siliceous ore, 2d class ore, conc. slime
12 (?)	10"	2'	4" brick 17" ore	9"	24"	21 1/2"	18"	25"
12 (?)	10"	2' 3"	5" brick 20 1/2" ore	24"	24"	26"	27"	31"
12 (?)	10"	2'	4" brick 19" ore	18"	18"	26"	20"	31"
5 (?)	4"	15"-18"	22" ore	32"	18"	20"	24"	31"
5 (?)	4"	15"-18"	20" ore	36"	14"	20"	17"	31"
11 1 1/2"	11	16 in. use 14 1 1/2"	10 1 1/2"	14 1 1/2"	14 1 1/2"	16 1"	14 1 1/2"	16 1 1/2"
.....	.....	3"-4"	6"	6"	6"	4 1/2"	8"	6"
2,000	7,000	5,000	3-4 charges of 5,000 lb. to white metal and this to blister copper	18,000 -20,000 20,000 -24,000	8,000	9,000	7,000	12,000
.....	.....	10,000	.....	.....	16,000	20,000	10,000 -14,000	17,000
20-40	90	40-50	400	200-250	90	45-55	120 & 135	135
16 (?)	12	7-9	3 1/2-4	6-7	12	13 & 18	6	9
7 1/2	5 1/2	10-15	10	12	9 1/2	13	8-10	16
20-25	51	28	33-35	45	40	20 & 37	40 & 51	44
16 (?)	.....	2-3	3-4	3	3	2 & 3.7	3, 40% Cu 4, 50% Cu 5, 60% Cu	5 1/2 with siliceous ore, 4 1/2 with 2d class ore
.....	.....	11-12	4.27	15	7.5	13.47 & 27	12, 40% Cu 16, 50% Cu 20, 60% Cu	18.8 with siliceous ore, 15.63 with 2d class
.....	.....	Converting 9, lining 7	19	Converting 7, relining 5	15	15	6 & 6	342
.....	.....	2	4	2	3	2	2	12-14
.....	.....	.....	15	6	10	.....	.....	36

the discharge of slag and blister copper on one side; on the opposite is the air-box, *e*, receiving the blast through pipe, *f*, and delivering it to the interior through tuyère openings, *g*, traversing the lining. The shell, *A*, is made up of four parts: the upper, *a*, forming the hood or head, carries at the lower end a cast-iron collar which serves for bolting it to the trunnion-ring that encloses the middle part, *a'*, of the shell; the lower part, *a''*, is similarly connected above to the trunnion-ring



FIGS. 322-324.—Upright converter of Great Falls, 1892-1904.

and below to the bottom part, *a'''*. Air-box, *e*, has opposite each tuyère an opening, *e'*, closed by a valve, to permit punching the tuyères. The peculiar form of the cavity is due to the uneven wear of the lining in converting (p. 311).

The converter is 7.5 ft. in diameter and 14 ft. 2 1/4 in. high, has a cylindrical body 8 ft. high, a cavity which takes an initial charge of 5 tons of 50-per cent.



matte and a final charge of 10 tons. The leading changes that have been made since then are assembled in Table 68.<sup>1</sup> The body was first lengthened and made elliptical;<sup>2</sup> this cross-section was retained and the length of the body further increased to 12 ft.; the elliptical cross-section had to give way again to the circular, while the increased length was retained, giving the present (1911) converter 12 ft. high and 12 ft. in diameter. The lining, now made of ore, is especially thick so that the initial charge is only 8500 lb. of 40-50 per cent. matte, while the final charge reaches 18,500 lb.

**160. Horizontal (David-Manhes, Leghorn, Trough, Barrel) Converter.**—In 1883 David and Manhès constructed at Egulles this second form of con-

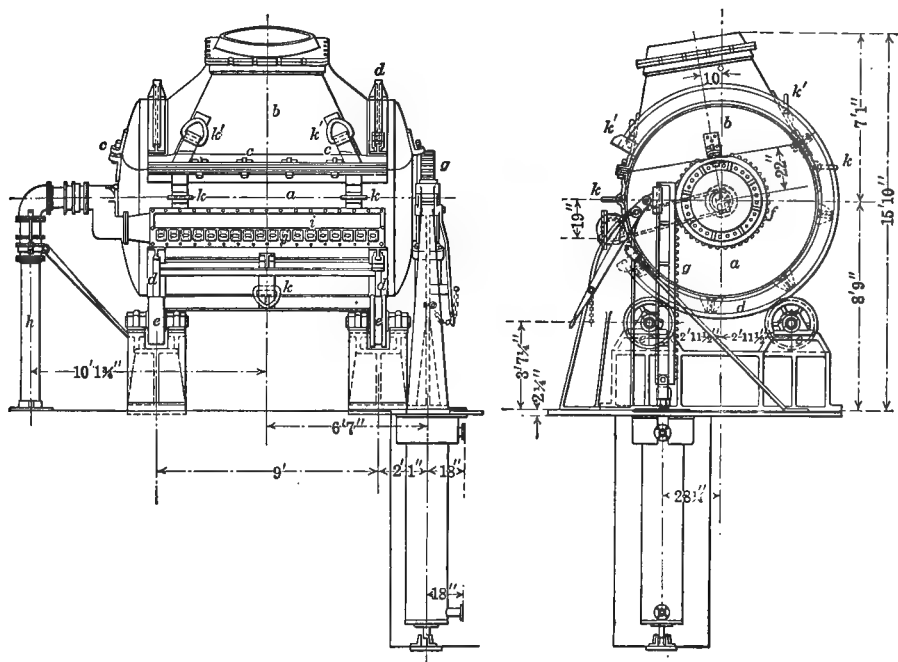


FIG. 325-326.—Horizontal converter of Anaconda.

verter, a horizontal cylindrical vessel, with lateral tuyères, resting and revolving in a horizontal plane on rollers. This has become the prototype of many modern converters. It was soon introduced at Leghorn, Italy; in 1891 it was in operation at Jeres Lanteira, Spain.<sup>3</sup> The leading facts are given in Table 68. The first horizontal converter in the United States for treating copper matte was that of the Copper Queen smelter.<sup>4</sup> This converter was larger than the others. Details are given in Table 68 as are the dimensions and working results of

<sup>1</sup> A complete discussion with drawings is furnished by Wheeler-Krejci, *loc. cit.*

<sup>2</sup> Elliptical Converter, *Eng. Min. J.*, 1906; LXXXI, 92.

<sup>3</sup> Massia, *Eng. Min. J.*, 1891, LII, 307.

<sup>4</sup> Douglas, *Tr. Inst. Min. Met.*, 1899-90, VIII, 2; *Tr. A. I. M. E.*, 1899, XXIX, 538.

some of the leading acid converters of the United States in operation in 1911. The history of American converters has been outlined by Christensen.<sup>1</sup>

THE ANACONDA CONVERTER of 1911<sup>2</sup> represented in Figs. 325-326, may serve as an example of this type. The boiler-iron shell, 12.5 ft. long and 8 ft. in diameter, consists of two parts, the barrel, *a*, and the hood, *b* (sometimes of cast steel), which are joined by key-bolts, *c*. The barrel rests with rail-shaped runners, *d*, upon two pairs of friction rollers, *e*, and is rotated at one end by a pinion, *f*, and vertical rack, *g*, operated by hydraulic power under a pressure of 400 lb. per square inch. At the other end is the blast-inlet pipe, *h*, delivering air under a pressure of 15 lb. to the air-box; whence it passes through 18 tuyères, *j*, provided with Dyblie ball-valves, into the cavity. Barrel and hood are provided with hooks, *k*, and *k'*, for raising by means of an overhead crane and transferring to the place for lining.<sup>3</sup>

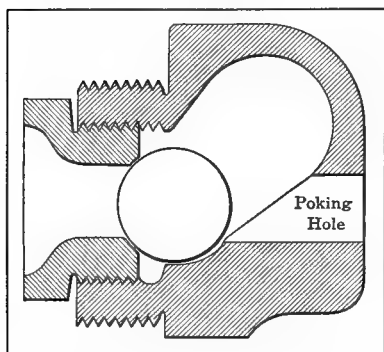


FIG. 327.—Dyblie tuyère-valve.

With more recent converters, *e.g.*, the Balaklava<sup>4</sup> (Table 68), the sides of the body are tangential to the cylindrical bottom. This gives a high horizontal parting line between body and hood, lying above the riding rings.

With most converters the individual tuyère is provided with a Dyblie valve, Fig. 327, which closes the poking-hole in the air-box opposite the tuyère. Each tuyère is usually attached to the wind-box with nipples and unions having brass seats; its discharge-end projects several inches into the shell and is screwed to the shell through a cast-steel stuffing-box.<sup>5</sup>

The principal modifications of the horizontal converter are those of Shelby, Haas, and David.

THE SHELBY BALL CONVERTER<sup>6</sup> which was in operation at Cerro de Pasco, Peru, is shown in Figs. 328-333. It is spherical, 11 ft. in diameter; the body is of boiler iron and has cast riding-rings, 8 ft.  $9\frac{1}{8}$  in. apart; the hood is of cast steel with riding-rings corresponding to those of the body. This electrically-driven converter fits into the stand of a barrel converter 11 ft. long and 8 ft. in diameter. The shell of the body reaches up high so that the parting line between body and hood (called head) is as far away as possible from the corroding and disintegrat-

<sup>1</sup> *Min. World*, 1910, XXXIII, 1036.

<sup>2</sup> Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 302.

Austin, *op. cit.*, 1906, XXXVII, 474.

Offerhaus, *Eng. Min. J.*, 1908, LXXXVI, 747.

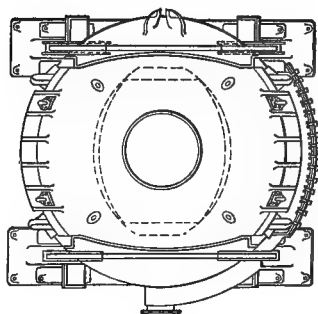
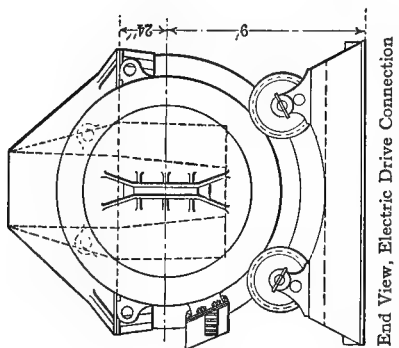
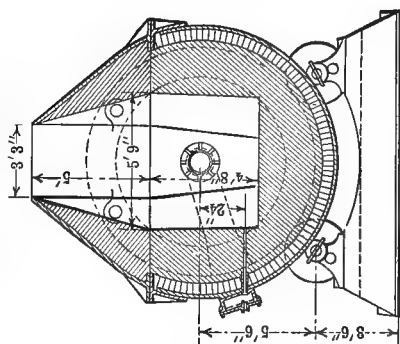
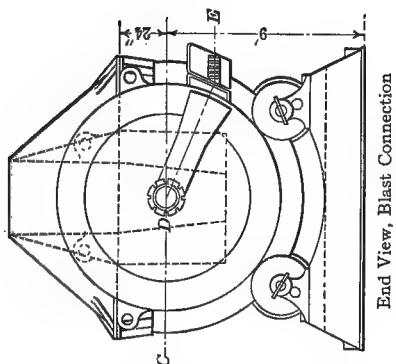
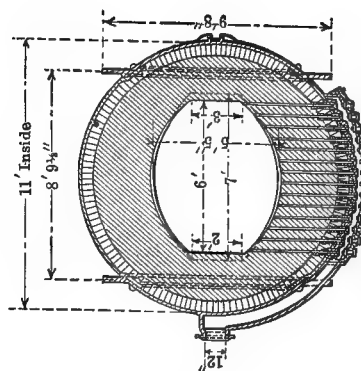
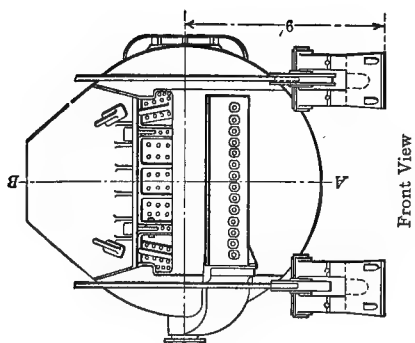
<sup>3</sup> Shelby's hook for crown, *Eng. Min. J.*, 1907, LXXXIV, 211.

<sup>4</sup> *Min. World*, 1910, XXXIII, 1037.

<sup>5</sup> Shelby, "Cananea Converter-valve," *Eng. Min. J.*, 1907, LXXXIII, 854.

<sup>6</sup> Shelby, *Eng. Min. J.*, 1909, LXXXVIII, 815, 1910; LXXXIX, 254.

Haas, *op. cit.*, 1909, LXXXVIII, 1033.



FIGS 328-333.—Shelby ball converter.

ing action of the charge. The main advantages of this ball over the usual barrel-type are: that the lining efficiency is two and one-half times as large, or two and one-half times as much copper can be produced on one lining as with the barrel-type, 11 ft. long and 8 ft. in diameter; and that larger initial and subsequent charges can be blown on account of the elliptical form of the cavity as against the usual rectangular, and on account of the more even wear of the smaller amount of lining required at the start.

THE HAAS VORTEX CONVERTER<sup>1</sup> combines some of the features of the ball and David types; an improvement designed in 1913 is a mechanical tuyère-punching device.<sup>2</sup>

THE DAVID SELECTEUR<sup>3</sup> is shown in vertical section in Fig. 334. The leading characteristics are: (1) That it is spherical and revolves on an inclined axis; (2) that it is bottom-blown with tuyères arranged in a circle and ascending at

an acute angle from the vertical, which is said to give the charge a rotary motion causing an even wear of the lining, and to render the tuyères more accessible for punching; and (3) that it has a pocket, *C-b'*, on the side, in which the metallic copper, first produced during the blister-stage of blowing, can be collected by turning down the vessel, and tapped through hole *h*. By producing about 10 per cent. bottom, as in the selecting process (§ 155), which carries with it impurities, the regule remaining in the converter is purified, and furnishes, when blown further, a high-grade blister copper.

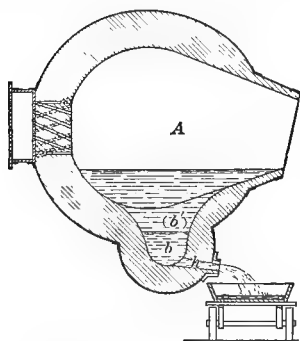


FIG. 334.—David selecteur.

The converter has not found any general application. The principle of removing the first Cu formed is in use at Wallaroo, Australia, and the O. K. mine, Northern Queensland,<sup>4</sup> where it is tapped when enough has been formed to collect the impurities of the matte.

**161. Upright versus Horizontal Converters.**—The tendency in this country has been away from the upright toward the horizontal converter notwithstanding the fact that the lining lasts longer and that the work leaves nothing to be desired as regards the bringing-forward of the matte. The original claim for the horizontal converter, that the depth of matte could be regulated by a change of position of the tuyère-level, and thereby the work carried on with a blast of lower pressure, is nugatory, as for an efficient utilization of the blast it is essential to have a deep bath of matte. The common practice with the horizontal converter is to turn it down as far as possible in order to secure a deep bath of

<sup>1</sup> *Min. Sc. Press*, 1908, xcvi, 469; *Eng. Min. J.*, 1910, lxxxix, 972, 1049; *A. I. M. E.*, Bull. 83, Nov., 1913, and 86, Feb., 1914.

<sup>2</sup> *Bull.* 83, *A. I. M. E.*, Nov., 1913, p. 2644.

<sup>3</sup> Burthe, *Ann. Min.*, 1898, xiii, 621; *Eng. Min. J.*, 1898, lxvi, 487; *Berg. Hüttenm. Z.* 1898, lvii, 366.

<sup>4</sup> Selby-Davidson, *Eng. Min. J.*, 1914, xcvi, 357.

matte. The main advantage of the horizontal converter appears in smaller height, greater accessibility, and ease of manipulation. Since the advent of the basic converter, the upright form is taking the place of the horizontal in the new installations.<sup>1</sup>

**162. Manipulation.**<sup>2</sup>—The early small converters were tilted by means of a lever, later by a worm-wheel; with increase in size of vessel hydraulic power came into use, operating a rack engaging with a pinion attached to one of the trunnions. The converter of Aguas Calientes, Fig. 321, has a horizontal rack, but this requires a special frame for the horizontal hydraulic cylinder, which complicates matters. More recent converters therefore adopted a vertical rack with hydraulic cylinder in a pit. Hydraulic power requires a high-pressure pump, an accumulator, and much piping; pipes, valves, etc.; these are subject to shocks, require repairs and duplication of parts; there is likely to be much leakage of water, as well as leakage and condensation of steam due to the intermittent work of the pumps. The whole installation is expensive and has been largely replaced by electric power. Every modern plant has an electric power system. A motor starts gently without a jar and moves smoothly, both of which are favorable to the life of the lining, and obviate the danger of splashing molten charge.

On account of the variable load due to intermittent working of cranes, locomotives, elevators, etc., the generator operates a large part of the time with a load insufficient for best economy. It can usually carry the extra load required to tilt the converter, or needs only little enlargement to do this additional work. The earliest electric installation is probably that of Great Falls in 1904. The 20-ft. upright basic converter,<sup>3</sup> Figs. 379–381, which weighs 65 tons excluding bearings and gearing, is operated by means of a 100-h.p. Westinghouse, type M.C., direct-current motor. The horizontal basic converter at Tooele is driven by a similar motor. One of the early electrically driven converters is that of the Orford Copper Co.,<sup>4</sup> where each barrel, 48×126 in., is provided with a 30-h.p. motor. Each motor makes 600 r.p.m. and is geared to a main shaft so that the greatest speed of the converter shell is reduced to 1.5 r.p.m. The direct-current motors used at first are being replaced by alternating-current types. Usually the motor is geared to a jack-shaft which drives the large gear of the converter through a worm-gear. The motors are inclosed to make them dust-proof, or they are placed in a sheet-iron housing which makes unnecessary the totally-enclosed motor. A motor is provided with an electric brake which works automatically as soon as the current is shut off.

Placing the converter in and removing it from the stand, that it may be repaired, used to be accomplished<sup>5</sup> by means of a low car with platform which was

<sup>1</sup> *Eng. Min. J.*, 1913, xcv, 335.

<sup>2</sup> Glasser, *Eng. Min. J.*, 1904, LXXVII, 437; "Electric Converter," *op cit.*, 1907, LXXXIII, 949 (Allis-Chalmers), 1913, xcv, 901 of Tooele (Rosenblatt); *Electrochem. Met. Ind.*, 1907, v, 244, 274 (Shipley); *Tr. A. I. M. E.*, 1913, XLVI, 486 of Great Falls (Wheeler-Krejci).

<sup>3</sup> Rosenblatt, *Eng. Min. J.*, 1913, xcv, 901.

<sup>4</sup> *Eng. Min. J.*, 1907, LXXXIII, 949.

<sup>5</sup> Copper Queen, Douglas, *Tr. Inst. Min. Met.*, 1899–90, VIII, pl. x; also at Aguas Calientes.

raised by means of a hydraulic piston. In all modern plants converters are exchanged through an overhead electric traveling crane, the capacity of which is made 50 per cent. larger than the heaviest piece it may be called upon to raise and transport.

**163. The Lining.**—The essential requirements of an acid lining are that it shall contain the largest possible amount of uncombined  $\text{SiO}_2$  that is consistent with its being mechanically strong. Free  $\text{SiO}_2$  is essential for the union with  $\text{FeO}$  as soon as formed; a clayey bond is equally necessary to hold together the particles of  $\text{SiO}_2$ . At first great stress was laid upon the refractoriness of the lining. Thus quartzite, crushed to pea-size, was mixed in an edge-roller pan with about 15 per cent. fire-clay for the body, and with about 20 per cent. for the hood, the relative amounts varying with the plasticity of the clay. Later, in order to cheapen the mixture, non-refractory clays were substituted, and often proved to be as satisfactory as the refractory.

The first to employ an ore containing metallic values was Hixon who in the 90's at Aguas Calientes employed as lining silver ore from Pachuca which contained the necessary free  $\text{SiO}_2$  and bonding clay-substance. The ore-lining was smelted without cost. His example was followed by others, low-grade siliceous ores were substituted for quartzite, and concentrator slimes having binding power for clay. The lining thus obtained is neither chemically nor mechanically as desirable as a quartz-clay mixture; but as it is smelted for nothing, the final return was so much greater, that this mode of procedure has become the common practice wherever it is at all practicable.

The fine-crushing and mixing of the components are usually carried on in a Chile mill. The size to which the ore ought to be reduced depends upon the amounts of fines produced in the comminution. These ought to be of such a character as to fill the interstices between the coarser grains. The coarsest grain will range from  $\frac{1}{2}$  to  $\frac{5}{8}$  in. Some mixtures used in the Boston & Montana works<sup>1</sup> at Great Falls are  $\text{SiO}_2$  88.6,  $\text{Fe}_2\text{O}_3$  3.1,  $\text{Al}_2\text{O}_3$  4.0,  $\text{CaO}$  1.6; Insol. 82.2,  $\text{SiO}_2$  63.0,  $\text{Fe}$  5.9,  $\text{Al}_2\text{O}_3$  17.3,  $\text{CaO}$  1.5,  $\text{MgO}$  1.3,  $\text{S}$  2.1,  $\text{Cu}$  1.0,  $\text{H}_2\text{O}$  11.0, Ignition loss 4.1;  $\text{SiO}_2$  85.0,  $\text{Fe}$  3.3,  $\text{Al}_2\text{O}_3$  4.0,  $\text{S}$  3.0,  $\text{Cu}$  4.0,  $\text{Ag}$  12 oz. per ton.

In recent years copper precipitate, from the treatment of mine-waters with iron, has been incorporated in the mixture of Montana linings, as in the ore-furnace it makes the matte too rich and in the refining furnace the metal too arsenical. At Anaconda in 1911 there were used the following mixtures: (1) 79 per cent. siliceous ore ( $\text{SiO}_2$  80.98,  $\text{FeO}$  3.68,  $\text{S}$  1.73,  $\text{Al}_2\text{O}_3$  4.19,  $\text{CaO}$  0.59), 21 per cent. concentrator slime ( $\text{SiO}_2$  56.25,  $\text{FeO}$  6.62,  $\text{S}$  7.39,  $\text{Al}_2\text{O}_3$  14.45,  $\text{CaO}$  0.72), furnishing a lining with  $\text{SiO}_2$  75.68,  $\text{FeO}$  4.30,  $\text{S}$  2.93,  $\text{Al}_2\text{O}_3$  6.40,  $\text{CaO}$  0.61 per cent.; (2) 29.4 per cent. lining-ore ( $\text{SiO}_2$  78.72,  $\text{FeO}$  3.71,  $\text{S}$  2.20,  $\text{Al}_2\text{O}_3$  5.44,  $\text{CaO}$  0.44); 55.1 per cent. second-class ore ( $\text{SiO}_2$  59.15,  $\text{FeO}$  11.28,  $\text{S}$  11.34,  $\text{Al}_2\text{O}_3$  9.46,  $\text{CaO}$  0.66), and 15.5 per cent. concentrator-slime ( $\text{SiO}_2$  56.62,  $\text{FeO}$  6.98,  $\text{S}$  7.79,  $\text{Al}_2\text{O}_3$  13.59,  $\text{CaO}$  0.64), furnishing a lining with  $\text{SiO}_2$

<sup>1</sup> Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 305.  
Wheeler-Krejci, *op. cit.*, 1913, XLVI.

64.40, FeO 8.40, S 8.13,  $\text{Al}_2\text{O}_3$  9.01, CaO 0.62 per cent. At Cananea<sup>1</sup> the barrel converter,  $96 \times 135$  in., is lined with 103 tons of ore-mixture of the composition  $\text{H}_2\text{O}$  5.60,  $\text{SiO}_2$  56.00,  $\text{Al}_2\text{O}_3$  14.20, FeO 5.40, CaO 1.70, S 5.5 Cu 2.49 per cent. The mixture runs very high in  $\text{SiO}_2$  and correspondingly low in  $\text{Al}_2\text{O}_3$ , but it makes a strong lining.

THE FORM OF THE CAVITY and the thickness of the lining show much variety, (Table 68). Fig. 335 gives a vertical section through the Great Falls converter of 1904. The cross-hatched part shows the form of lining of 1904, the dotted line the one used at first. Formerly the 3-ft. cavity was placed in the center of the shell and the lining rammed around it symmetrically. It was found, however, that at the tuyère-level the lining was slagged much more quickly at the tuyère-side than on the pouring-side, and that at the level where the hood starts, the mechanical wear was greater on the pouring- than on the tuyère-side. Therefore the base of the cavity was placed nearer the pouring-side to give the lining at the tuyères a greater thickness, and the cavity was made to slant toward the tuyère-side with a thickening of the lining on the upper pouring-side. Table 68 shows that at Aguas Calientes the cavity has retained its central position.

The rammed lining of horizontal converters shows a greater diversity of form than does that of the vertical. The shell of most horizontal converters is protected from wear by a half or a full course of brick on which is rammed the mixture that is exposed to chemical and mechanical wear. Figs. 336–337 show the peculiar form of the lining of the Butte & Boston horizontal converter, Figs. 338–339, the section most common with horizontal converters, and Fig. 340 the symmetrical arrangement of the Anaconda converter. Table 68 gives the leading dimensions of the linings of some of the principle barrel converters of the United States.

Body and hood are rammed separately. Machines similar to air-drills, first introduced<sup>2</sup> at Great Falls in 1896, are usually employed. Fig. 341 represents the machine used at Anaconda for ramming the lining;<sup>3</sup> *a* is an Ingersoll-Sergeant tamping machine, 5-in. diameter and 20-in. stroke, operating at 50 lb.

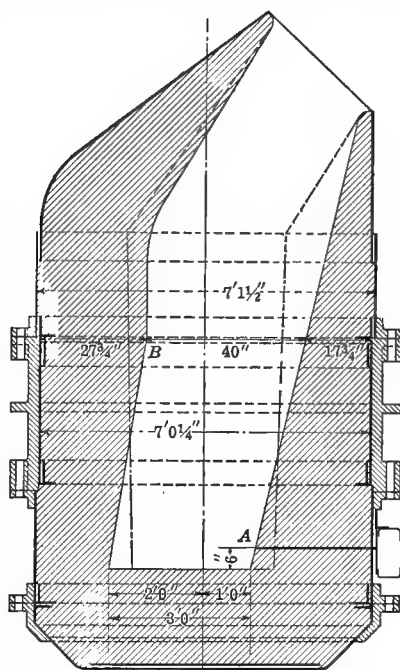


FIG. 335.—Lining of Great Falls upright converter of 1904.

<sup>1</sup> DeKalb, *Min. Sci. Press*, 1910, CI, 11.

<sup>2</sup> Wheeler-Krejci, *Tr. A. I. M. E.*, 1913, XLVI, 498.

<sup>3</sup> See also Shelby, *Eng. Min. J.*, 1908, LXXXVI, 749.

pressure, suspended from a carriage carried by a revolving gib-crane, *b*, which is attached to an hydraulic piston and counterpoised to give vertical motion. The lining material is dumped from wheelbarrows into the shell and rammed solid in thin layers to the level of the cavity, when the core-mold is put in place and the space between it and the shell filled gradually and rammed. The

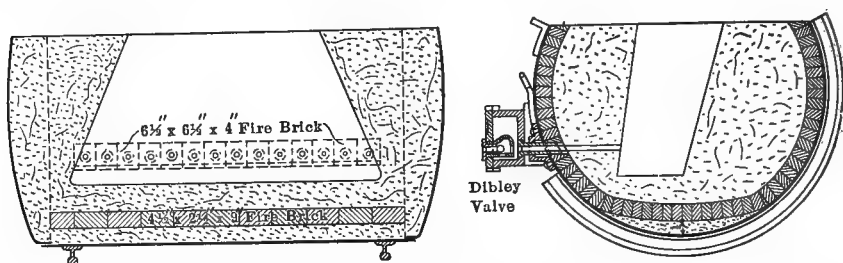


FIG. 336-337.—Butte & Boston horizontal converter, sections of lining and Dyblie valve.

mold, usually of steel plate, is made of several pieces; some of these are wedge-shaped to make possible the removal. When the lining is finished, the holes for the tuyère-openings are punched through it.

The hood is inverted and lined, either as is the body by machinery, or occasionally by hand, when balls of mixture are beaten-down against the shell,

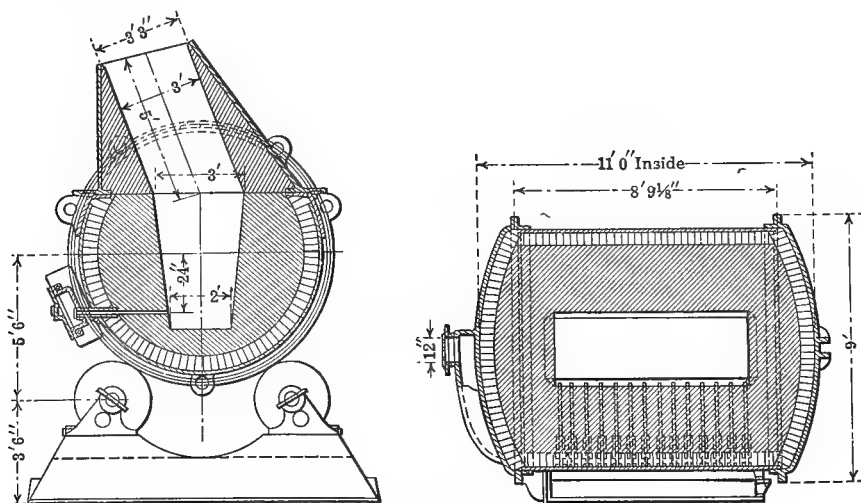


FIG. 338-339.—Usual form of lining in horizontal converter.

which is provided with iron spirals to hold the lining. The top of the lining of the body is now covered with balls of clay which serve to form a tight joint with the hood when this is lowered in place and keyed fast. The work of lining is usually done by contract, a premium being given for a lining that produces more than a fixed amount of copper.



A lining put in with power has a longer life than one put in by hand. An average of two years' work in 1895 by hand- and in 1896 by machine-tamping has been recorded by Wheeler and Krejci.<sup>1</sup> The average figures are given in Table 69.

TABLE 69.—COMPARISON OF HAND- AND MACHINE-TAMPING OF CONVERTER-LINING

Grade of matte, per cent. copper		Lb. copper produced per lining		Tons lining per ton copper produced	
1895 Hand	1896 Machine	1895 Hand	1896 Machine	1895 Hand	1896 Machine
47.9	54.3	25,818	31,443	0.581	0.457

Although the grade of matte was higher after April 1, 1896, than before, the difference is not sufficiently great to account for the increased production of copper per lining, and the decreased consumption of lining per ton copper produced.

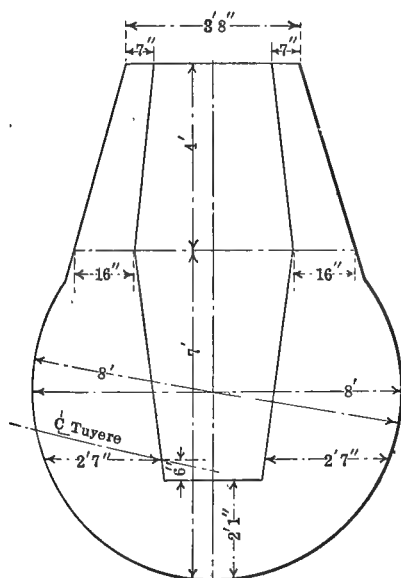


FIG. 340.—Lining of Anaconda horizontal converter.

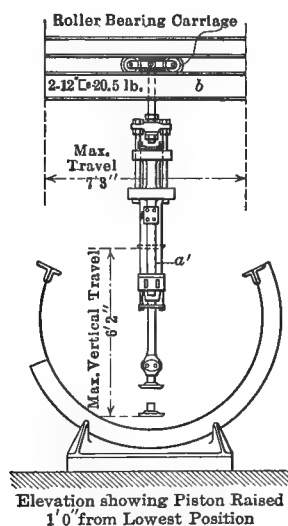


FIG. 341.—Machine for ramming converter lining.

The rammed converter has now to be dried, warmed, and heated. This is done by having a wood fire, followed by the burning of coke or coal, the air necessary being supplied through the tuyères. From 1 to 2 tons of coal or coke are thus consumed in from 8 to 24 hr. H. L. Charles<sup>2</sup> patented a method for

<sup>1</sup> *Tr. A. I. M. E.*, 1913, XLVI, 500.

<sup>2</sup> *Min. Sc. Press*, 1907, XCIV, 572; *Eng. Min. J.*, 1907, LXXXIII, 1046; *Min. Reporter*, 1907, LV, 378; *Min. World*, 1907, XXVI, 448, 478.

getting ready a freshly-lined converter; it consists (1) in filling the converter with slag, preferably converter-slag, after the punched tuyère-holes have been plugged from the inside with a stiff clay; (2) in allowing it to stand filled for 1 to 3 hr.; (3) in emptying the contents and allowing the slag-shell formed to cool gradually. A number of vent holes have to be provided in the shell for the escape of water-vapor. The cavity has to be from 2 to 3 in. wider and deeper than usual to furnish room for the slag-shell. The tuyère-openings are punched through the slag. It is claimed that with this method the life of the lining is prolonged for from one to three charges.

**164. The Blast.**—The blast for the converter attains a pressure of 16 lb., and the air consumption can be placed at 200,000 cu. ft. per ton of copper.<sup>1</sup> In one of the largest plants of the United States the official figure is 183,000 cu. ft. of air per 2000 lb. copper or 5713 cu. m. per 1000 kg.; 1 i.h.p. is required to furnish the air for every 4.88 lb. Cu produced. Sticht<sup>2</sup> states that at Mount Lyell for 1 long ton Cu there are blown with 50-per-cent. matte 100,000 cu. ft., and with 40-per-cent. matte 165,000 cu. ft.

Taking a matte with Cu 45, Fe 30, S 20 as typical, calculation shows that there are required for 1,000 kg. Cu 3173.33 kg. air. The above 5713 cu. m. air, with a mean temperature of 20° C. at an altitude of 5000 ft. (=635 mm. Hg), reduced to 0° C. and 760 mm. Hg.=5752 kg., hence the efficiency of the blast supplied is only  $3173:5752=0.5516=55.16$  per cent. Considering that in converting, free O appears in the gases only toward the end of the blister-forming stage, the efficiency figure of 55.16 per cent. appears exceedingly low. Moore<sup>3</sup> determined the efficiency in a given plant at 74 per cent. The losses are due to temperature and moisture of the air, leakage in air-cylinder, valves, pipes, tuyères, cracks in lining, punching, etc.

The usual reciprocating air-compressor is giving way to the compound turbo-blowing engine.

**165. Accessories.**<sup>4</sup>—Some of these are the hood, ladles for matte and slag, slag-casting machines, molds for copper, etc.

THE HOOD which conveys the converter-gases to the dust-flue used to be stationary; later it was made movable,<sup>5</sup> but one of the latest installations has returned again to the stationary type. The stationary hood of Brower and the movable hoods of Dorell and Laist-Tanner may serve as examples.

The hood of Brower in use at the works of the U. S. Metals Refining Co.,<sup>6</sup> Chrome, N. J., and shown in Figs. 342–346, consists of two steel castings which are bolted together and have attached to them the suspension frame. The latter is built of 6-in. channels, which rest on knee-brace supports of the building, and is provided with a loop for suspension by the hook of the traveling

<sup>1</sup> Haas, *Eng. Min. J.*, 1910, LXXXIX, 972.

<sup>2</sup> *Australasian Assoc. Adv. Science*, 1907, p. 35.

<sup>3</sup> *Eng. Min. J.*, 1910, XC, 462.

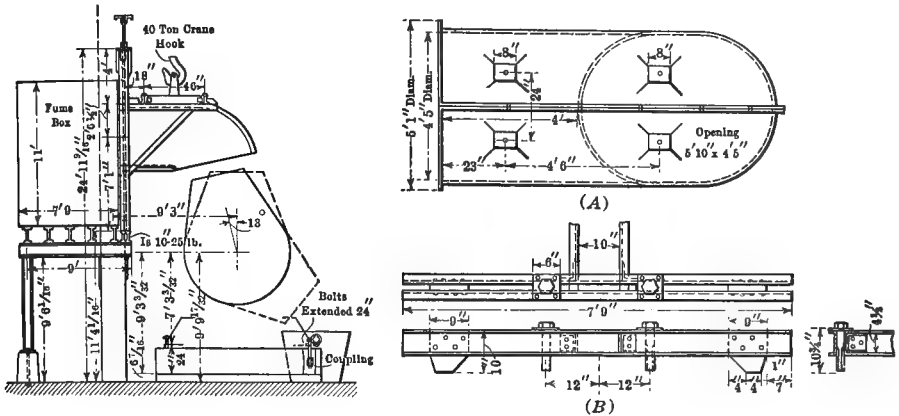
<sup>4</sup> Glasser, *Eng. Min. J.*, 1904, LXXVII, 519.

<sup>5</sup> Shelby, *Eng. Min. J.*, 1911, XCI, 311.

<sup>6</sup> Vail, *Eng. Min. J.*, 1913, XCV, 1031, 1247.

crane. When the hood is to be cleaned, it is transferred to the ground, and another put in its place.

The Dorell hood,<sup>1</sup> in use at the Butte Reduction Works until closed down, Fig. 347, is mounted on wheels and operated by an air-cylinder having a 6-ft.



FIGS 342-346.—Brower converter-hood.

stroke. When the converter is in operation, the hood covers the mouth completely; the gases enter it below at one end, leave it above at the other, and enter the main flue.

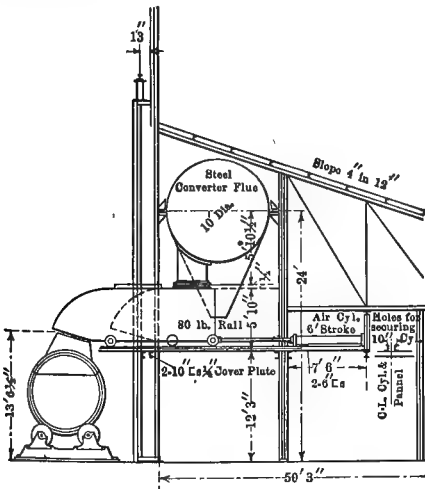


FIG. 347.—Dorell converter-hood.

The Laist-Tanner hood,<sup>2</sup> Fig. 348, also can be moved back and out of the way by a 12-in. air-cylinder when the converter is to be replaced. The end of the square flue in the backward posi-

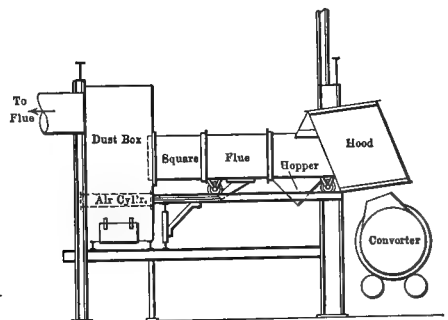


FIG. 348.—Laist-Tanner converter-hood.

tion butts against the back-wall of the chest-box and thus closes the outlet-flue. The square flue and dust-box have hoppers for withdrawing accumulated dust.

<sup>1</sup> Eng. Min. J., 1910, LXXXIX, 451.

<sup>2</sup> Min. Sc. Press, 1907, XCV, 400.

LADLES for slag and matte are the same as those discussed in connection with the disposal of blast-furnace products (§§ 95 and 96).

SLAG-CASTING MACHINES are found in large plants in which the converter-slag is to be resmelted in the blast-furnace. Such a machine is that of F. G. Kelley<sup>1</sup> in operation at Garfield and shown in cross-section in Fig. 349. The converter-slag arrives in a 5-ton ladle, is poured into one of 24 cast-iron molds standing in a row, each firmly connected with a steel frame bolted to a cast-iron rocker; the construction is such that the molds are in a horizontal position when empty, and in a dumping position when full and released. In Fig. 349 one frame is shown in a receiving, the other in a dumping position. A cast-iron mold, made up of four plates, is 10 ft. long, 4 ft. wide, and 4 in. deep; it is divided by ribs 2 in. high into four compartments, and holds 600 lb. of slag.

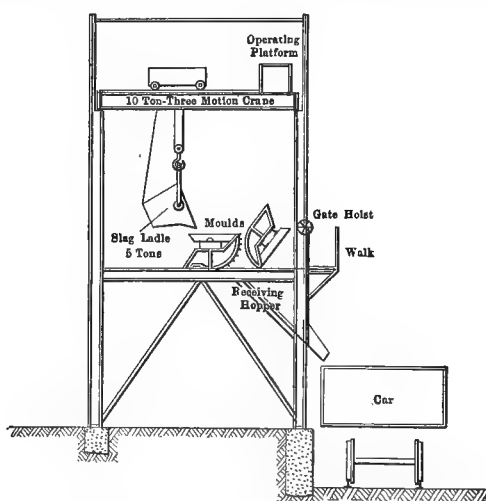


FIG. 349.—Kelley slag-casting machine.

The circular casting-machine, in operation at Great Falls, Mont.,<sup>2</sup> is shown in plan in Fig. 350. It consists of an annular turntable, *A*, 70 ft. in diameter, carrying 160 tilting molds, *B*, represented in section in Fig. 351. The table is driven like a pulley by a wire operated by two motors, *C* and *D*. The slag is brought from the converters in a ladle by an overhead electric crane, emptied into the 5-ton pouring-ladle *E*, which is similar to the one discussed in Figs. 353-354, and then cast through a curved spout into white-washed molds. When the filled molds arrive at the dumping pocket *F*, they are tilted automatically and discharge onto a steep grizzlie to break the cakes. The broken slag is hosed and collected in a bucket which is raised on the inclined skipway *G* and delivers the slag to a bin whence it is drawn into blast-furnace charging cars.

<sup>1</sup> *Eng. Min. J.*, 1908, LXXXVI, 610.

<sup>2</sup> *Wheeler-Krejci, Tr. A. I. M. E.*, 1913, XLVI, 508.

The slag-skulls are collected in the center of the table, broken, and shoveled into the skip. The blister copper from the converter is poured direct into molds at small plants. In order to prevent spattering, the Bennetts Pouring Spoon,<sup>1</sup> Fig. 352, is frequently used. The inside dimensions of a mold holding 200 lb. of copper are: length at top 24 in., at bottom 20 in., width at top  $9\frac{3}{4}$  in., at bottom  $5\frac{1}{4}$  in., depth  $5\frac{1}{2}$  in. The car carrying the molds<sup>2</sup> is constructed of I-beams or channels, and has roller-bearing wheels and axles. The rails should

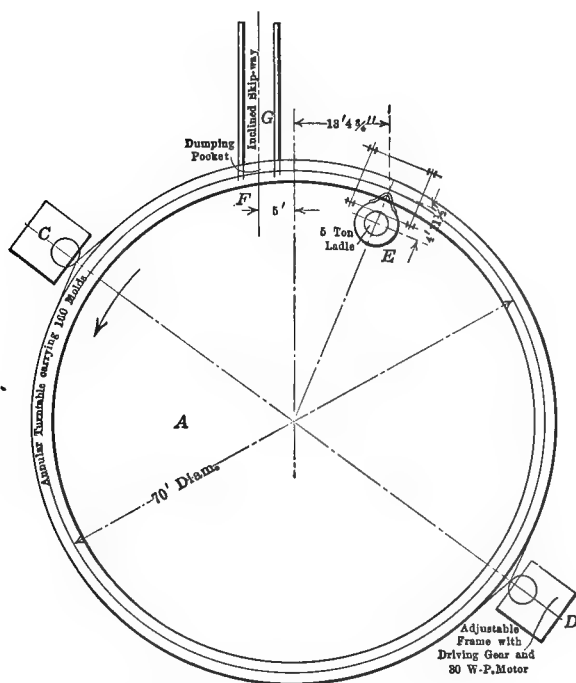


FIG. 350.—Great Falls converter-slag-casting machine.

not be less than 50-lb.; Shelby<sup>3</sup> advocates the use of cast-iron rails of  $\perp$ -section, 8-in. height, 6-in. base, 5-ft. length, laid in concrete.

In large plants the blister copper is poured from the converter into a ladle, thus leaving the converter free to be recharged with matte. The copper is molded with a casting machine.

The machine<sup>4</sup> in operation at Great Falls, Mont., since 1903, is shown in Figs. 353-354. This is a modified Walker machine (§ 194) with an electrically

<sup>1</sup> Allis-Chalmers Co., Milwaukee, Wis.

<sup>2</sup> Glasser, *op. cit.*; *Min. Mag.*, 1904, X, 135.

<sup>3</sup> *Eng. Min. J.*, 1907, LXXXIV, 499.

<sup>4</sup> Klepinger, *Eng. Min. J.*, 1908, LXXXV, 903.

Wheeler-Krejci, *Tr. A. I. M. E.*, 1913, XLVI, 497.

driven annular frame, 24 ft. in diameter, carrying 24 anode molds, or a correspondingly greater number of cake, bar, or ingot molds. The automatic tilting, the inverting of the mold over the sweep (bosh), and the reversing characteristic of the Walker machines are not shown in detail. The main novelty of the

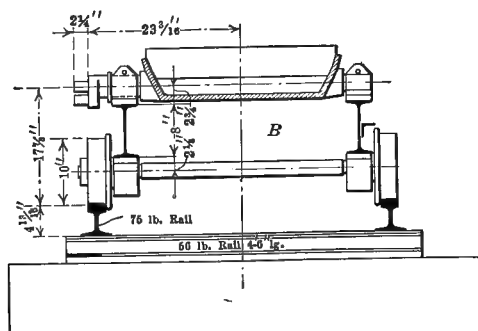


FIG. 351.—Great Falls converter-slag-casting machine.

apparatus lies in the pouring mechanism. The ladle containing the copper is placed by an overhead electric crane in the pouring apparatus which consists of an hydraulically-operated plunger carrying a frame with V-shaped pockets

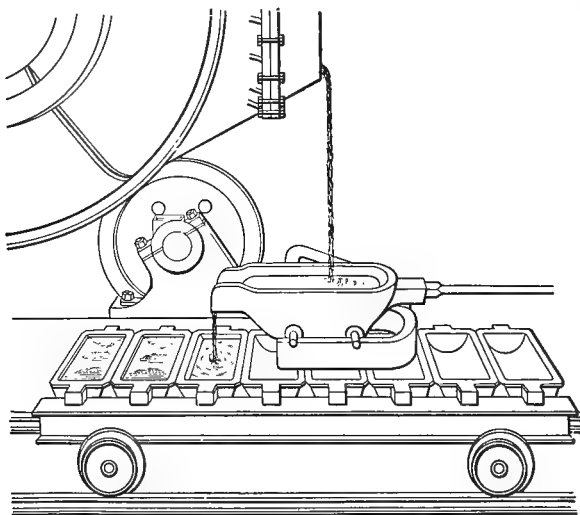


FIG. 352.—Bennetts pouring spoon.

for receiving the trunnions of the ladle, to be held in place by two wedges or keyes. The ladle-frame, pivoted on top of the plunger, is also suspended by links, so that upon raising the plunger and tilting the ladle forward, the ladle-spout remains a uniform distance from the mold. While the ladle passes from

its original position, when full, to its final position, when empty, the spout moves across the mold from front to back, and thus changes continuously the point at which the hot blister copper strikes the mold, and thereby lengthens

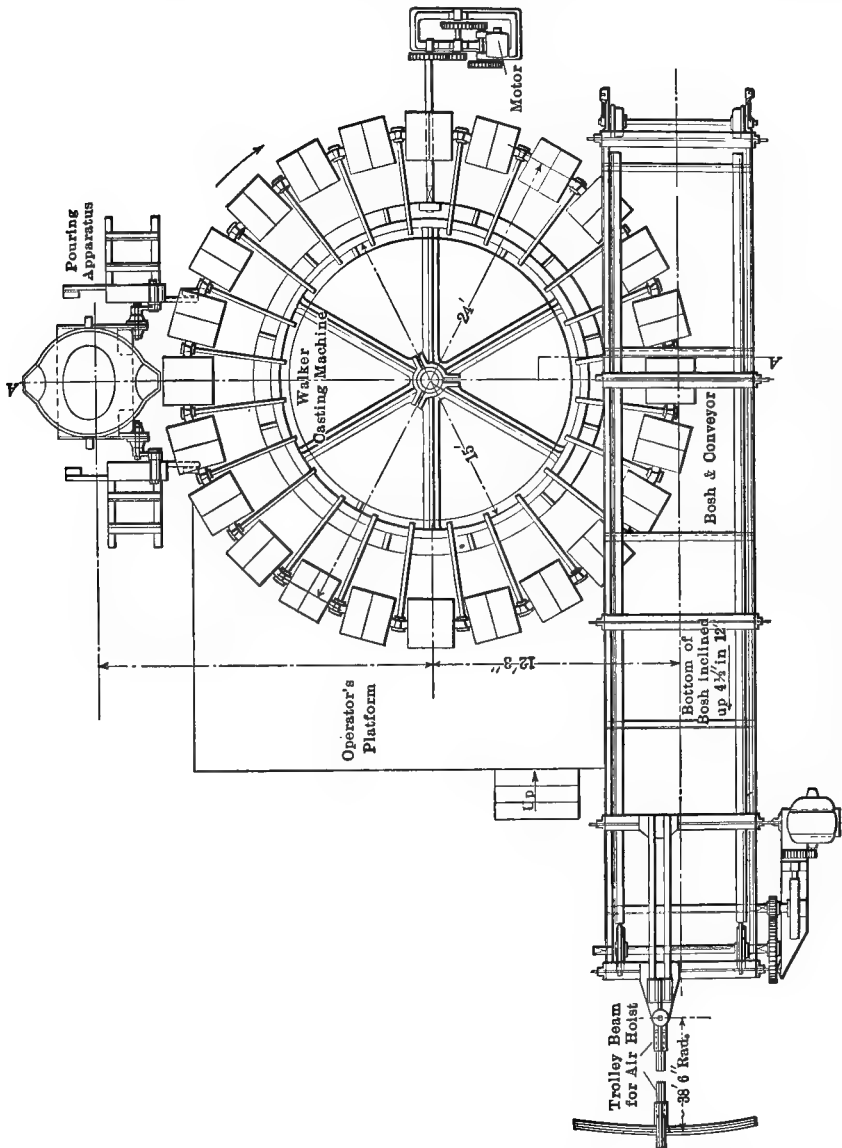


FIG. 353.—Klepinger copper-casting machine, Great Falls, Mont.

the life of the latter. The anodes are raised from the bosh by an endless conveyor which returns overhead. Over the discharge-end of the bosh are pivoted two trolley-beams, 38 ft. 6 in. long, running in a circular track at their outer ends. They are provided with air-hoists for picking up anodes and delivering

them within the space controlled by the beams. This is large enough to store all the copper produced between shipping periods. The machine handles 150 tons of metal in 12 hr. with only three men. Other casting machines are discussed in § 194.

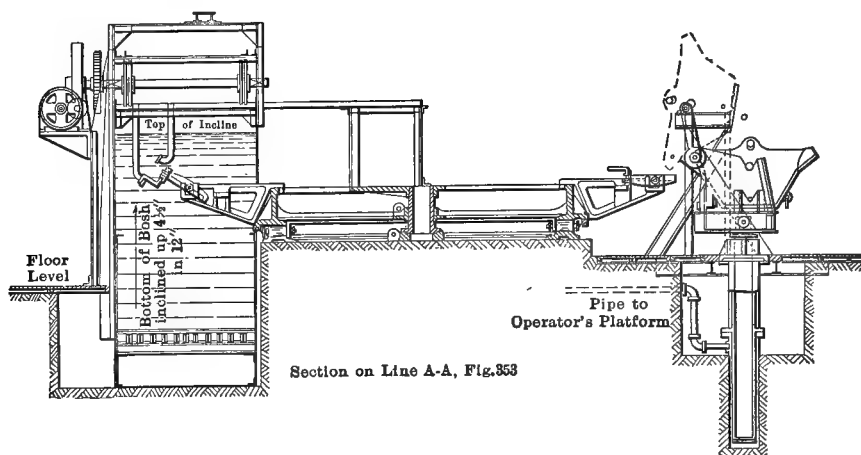


FIG. 354.—Klepinger copper-casting machine, Great Falls, Mont.

**166. Arrangement of Plant.**—In the early plants, cold matte was melted in a cupola, tapped and run direct into the converter. The use of CUPOLA-MATTE has been abandoned by most modern plants. At Mount Lyell matte is still remelted, as the grade obtained by the pure pyritic smelting varies too much in its copper-content to permit the use of matte direct from the settler of the blast-furnace, as is customary in plants carrying on partial pyritic smelting. Typical examples of early cupola-matte plants are the Parrott;<sup>1</sup> and the Old Anaconda.<sup>2</sup> The converting plant of Mount Lyell is described by Fawns<sup>3</sup> and Sticht.<sup>4</sup> One of the early cupolas described by Stickney<sup>5</sup> is shown in Fig. 355. It has a circular water-jacket shaft; a detached movable crucible lined with converter material to furnish a cavity holding a full converter-charge; a tuyère-region of lining material about 18 in. thick; a launder, 12 in. in diameter and lined, having a fall of 12.5 per cent. or more to insure a free flow of matte. It is suspended from a swinging crane by a chain-tackle. Matte in lump form is charged with 12 per cent. coke and some flux for the coke-ash. The small amount of slag (Cu 4-5 per cent.) formed is drawn from the crucible filled with matte when this is to be tapped. The furnace melts 30 tons of matte in 24 hr. with a moderate heat and requires two men on each shift.

In some DIRECT-MATTE plants conditions do occur in which the converter

<sup>1</sup> Peters, "Modern Copper Smelting," 1895, p. 540.

<sup>2</sup> Hixon, *op. cit.*, 1908, p. 95.

<sup>3</sup> *Tr. Inst. Min. Met.*, 1895-96, IV, 284.

<sup>4</sup> *Min. Ind.*, 1907, XVI, 437.

<sup>5</sup> *Op. cit.*, 1892, I, 152.



has to melt temporarily its own matte. Thus at Greenwood, B. C.,<sup>1</sup> the procedure with a barrel converter, 126×84 in., having at its disposal 4500 cu. ft. air at 10 lb. pressure, was as follows: a wood fire was started, then a charge of 1500 lb. coke given and a light blast used; 3 tons of cold matte was charged and full blast turned on. The matte fused quickly, more matte was added, the slag skimmed; again matte was charged; and so on until the converter was filled, when it was blown to blister copper. The time required from charging cold matte to obtaining blister copper was  $3\frac{1}{2}$  hr., 15 tons of 40- to 50-per-cent. matte were thus converted with one stand in a shift; 45-per cent. matte worked well;

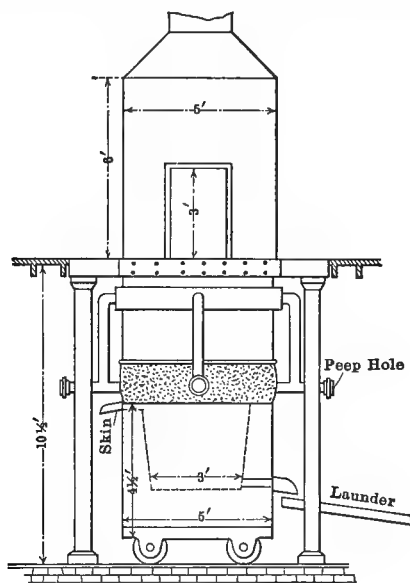


FIG. 355.—Matte cupola.

55-per-cent. matte required careful handling and occasional additions of coal to prevent freezing. If a converter cannot be run continuously, say for only 8 hours out of 24, it may be kept hot the remaining 16 hours by filling in the hot ashes from a reverberatory furnace.

In Direct-Matte plants the converters are always placed in a straight line. If the size of the works is not too great, the smelting and converting departments will be under a single roof, otherwise they are in separate buildings as, *e.g.*, at Anaconda. The plan and vertical cross-section of the smelting and converting departments of the Great Cobar smelting works<sup>2</sup> are shown in Figs. 356–357. The plant is built on level ground. There are three blast-furnaces, 56×240 in., arranged end to end, with settlers 18 ft. in diameter and 4 ft. deep, and served by three Connorsville pressure blowers, each of 300 cu. ft. capacity per revolution. The slag overflows into 25-ton ladles mounted on two 4-wheel trucks; the matte

<sup>1</sup> Jacobs, *Eng. Min. J.*, 1906, LXXXII, 440.

<sup>2</sup> Corresp. *Eng. Min. J.*, 1908, LXXXV, 952.

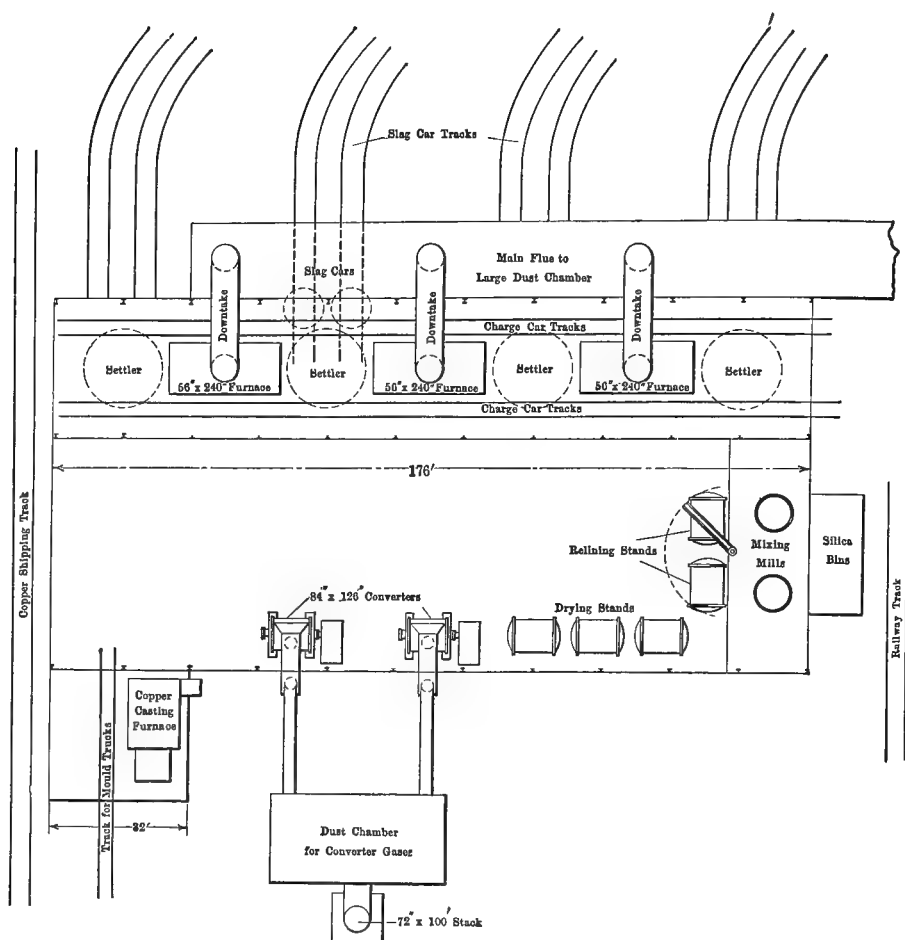


FIG. 356.—Blast-furnace and converter departments, Great Cobar, Australia.

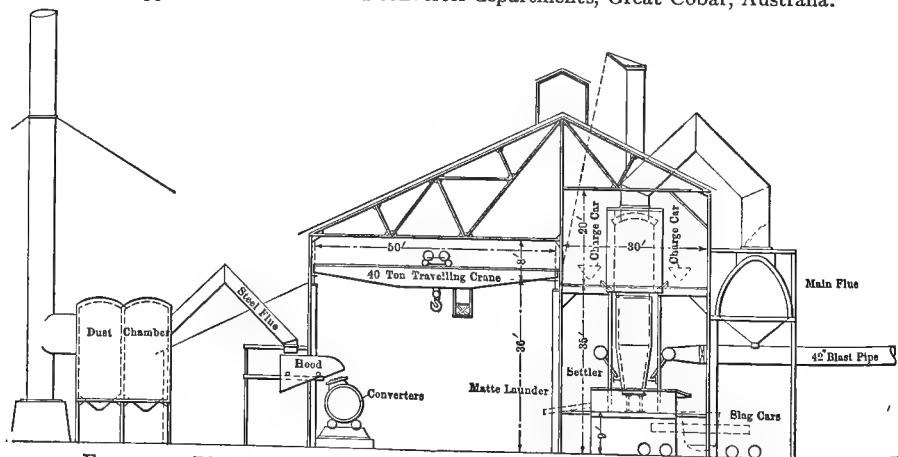


FIG. 357.—Blast-furnace and converter departments, Great Cobar, Australia.

is tapped into 10-ton ladles handled by a 40-ton electric traveling crane with 50-ft. span, and poured into the horizontal converters,  $84 \times 126$  in. There are two stands for blowing, three for drying, and two for relining; back of the last are the edge-roller mixing mills. Air is supplied to the converters by a duplex blowing-engine of 10,000 cu. ft. air per minute at 15 lb. terminal pressure. The blister copper is discharged into ladles and then poured into a 15-ton casting furnace, where it is refined and cast into anodes.

**167. Mode of Operating and Chemistry.**<sup>1</sup>—The matte entering a converter usually assays about Cu 45 per cent. This grade is satisfactory for obtaining a lean slag in the ore-smelting furnace, a high temperature in the converter, and a reasonable length of life for its lining. Taking a matte with Cu 30, Fe 40, S 30 per cent., for 1 part Cu about 1.7 parts FeO will have to be slagged; a matte with Cu 51, Fe 23, S 26 per cent., will give for 1 part Cu only 0.6 parts FeO, *i.e.*, the life of the lining will be more than doubled. Going higher than 50 per cent. is not advisable for mechanical reasons<sup>2</sup> and for the insufficiency of heat evolved to carry the process through to blister copper. However, under exceptional conditions, matte with 66 to 69 per cent. Cu has been successfully converted.<sup>3</sup>

Supposing a charge has been blown and the copper poured, the converter will be turned up sufficiently to have the mouth in the right position to receive a new charge of liquid matte. This will be poured in from a ladle or run in through a launder, full blast will be turned on, and the converter righted so that the mouth will deliver the gases into the hood. The blast penetrating the matte starts the process.

(1) THE SLAG-FORMING STAGE.—The main chemical reactions taking place are:  $\text{FeS} + 3\text{O} = \text{FeO} + \text{SO}_2$ ;  $2\text{FeO} + \text{SiO}_2 = \text{Fe}_2\text{SiO}_4$ ;  $\text{Cu}_2\text{S} + 3\text{O} = \text{Cu}_2\text{O} + \text{SO}_2$ ;  $\text{Cu}_2\text{O} + \text{FeS} = \text{Cu}_2\text{S} + \text{FeO}$ . The Fe is oxidized to FeO and simultaneously combines with the  $\text{SiO}_2$  of the lining. As the temperature of the matte-bath is about  $1200^\circ \text{C}$ ., the ferrous singulo-silicate is produced, the formation temperature of which lies at  $1270^\circ \text{C}$ . The matte upon entering the converter is at a lower temperature, averaging  $900^\circ \text{C}$ . at Anaconda.<sup>4</sup> Iron continues to be oxidized, any  $\text{Cu}_2\text{S}$  that may be oxidized is again sulphurized by the FeS that is present.

At the beginning of a blow, white fumes of  $\text{SO}_2$ , ZnO, PbO, etc., pass off; the flame issuing from the converter<sup>5</sup> is tinged rose, becomes greenish, and then turns pale blue.<sup>6</sup> The tuyères need punching at intervals to insure a free passage of air; a small jumping flame indicates the necessity of it.

<sup>1</sup> Parsons, *Eng. Min. J.*, 1897, LXIII, 481.

Moore, *op. cit.*, 1910, XC, 460.

<sup>2</sup> Schröder, *Met. Chem. Eng.*, 1910, VIII, 590.

<sup>3</sup> Longbottom, *op. cit.*, 1910, VIII, 426.

<sup>4</sup> Austin and Offerhaus, *loc. cit.*

<sup>5</sup> Levy, *Tr. Inst. Min. Met.* 1910-11, XX, 117; *Eng. Min. J.*, 1910, XC, 1207 (flame colors at Anaconda).

<sup>6</sup> In converting Cu-Ni matte the flame has an entirely different aspect. In fact, the presence or absence of some metals changes the character and succession of colors.

The duration of the slagging stage is about 60 min. for a charge of 7 to 9 tons of 45-per cent. matte. All the iron having been slagged, the converter is turned down, the blast shut off, the larger part of the slag poured and the rest skimmed into a ladle. The approach of white metal toward the rim of the mouth of the converter is ascertained by cutting the stream of slag with a rabble at the place where the white metal ought to appear first; it looks like sizzling grease under the smooth surface of the slag, and boils on the rabble, while the slag appears rather to adhere to it. The slag contains about 2.4 per cent. Cu; an average of one year's runs at Great Falls gave Lloyd  $\text{SiO}_2$  30, FeO 55,  $\text{Al}_2\text{O}_3$  9, CaO 1, Cu 2 per cent. Full blast is now turned on again, the converter righted, and with it is started

(2) THE BLISTER-FORMING STAGE.—The chemical reactions are:  $\text{Cu}_2\text{S} + 3\text{O} = \text{Cu}_2\text{O} + \text{SO}_2$ ;  $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} = 6\text{Cu} + \text{SO}_2$ ;  $2\text{Cu}_2\text{O} + \text{SiO}_2 = \text{Cu}_4\text{SiO}_4$  to a moderate degree. The white metal produced in the first stage is oxidized, and the  $\text{Cu}_2\text{O}$  formed reacts upon undecomposed  $\text{Cu}_2\text{S}$  as in the Welsh reverberatory-furnace process. Incidentally some  $\text{Cu}_2\text{O}$  is scorified. The flame, pale blue at the start, becomes bluish-white, rose-colored to reddish-brown, and disappears.

The indication of a finished charge is that the sparks thrown from the nose of the converter against the back of the hood cease to be dull, having become brilliant, and no longer adhere to the hood but rebound from it. The appearance of the Cu on the rod inserted into and quickly withdrawn from the converter clearly indicates the state of the metal. A sample poured on the floor may be underblown and contain matte; or overblown to reddish blister,\* to expel all the gas, when it will show pimples; or blown only to gas-finish, when  $\text{SO}_2$  will be given off freely upon solidifying; or to a partial set, when the surface of the sample will show a brown to blackish surface.

The tuyères need almost continual punching in order to furnish the air a free passage.

The time required with an initial charge of 7 to 9 tons of 45-per-cent. matte is from 60 to 90 min. When the charge is finished, the converter is turned down, the blast shut off, and the blister copper poured into ingot- or anode-molds, or into a lined ladle to be transferred to a casting-machine or a reverberatory refining furnace.

A wooden pole is usually inserted through the nose of the converter to hold back the slag; this slag assays at Anaconda<sup>1</sup>  $\text{SiO}_2$  22.7, Cu 21.43, FeO 39.4, S 0.04 per cent.

The white metal produced by the slag-forming stage is usually too hot for a satisfactory blow for blister copper; it is therefore cooled by adding "dope," *i.e.*, cold white metal, rich slags, old lining, cleanings from hood, dust chamber, floors, etc. If it is too cool, some coal will be charged; injecting warmed crude oil through the tuyères<sup>2</sup> at a pressure of 20 lb. has been a successful remedy at the works of the Mountain Copper Co. The use of air slightly enriched in

<sup>1</sup> Offerhaus, *loc. cit.*

<sup>2</sup> Rountree, *Eng. Min. J.*, 1907, LXXXIV, 639.

O has shown a striking effect in laboratory experiments.<sup>1</sup> The flame becoming reddish instead of being reddish-brown is an indication of the converter being too cool; the temperature is too high if the flame becomes yellow, and if at the same time there is encountered an excessive resistance in the punching of the tuyères.

The operation of "Doubling," *i.e.*, working two matte charges consecutively in one vessel before blowing for blister copper, is carried on for three reasons: If the temperature of the matte was too low, the slag-forming stage is unduly prolonged, and the white metal not entirely freed from FeS, so that the charge is in danger of freezing during the blister stage; hence another matte-charge is given which will prevent freezing. If the cavity of the converter has become large, it may be necessary to have two white-metal charges to obtain sufficient submersion of the tuyères; hence the white metal of one converter is often poured into that of another. If low-grade matte is being converted, the charge may have to be doubled to obtain the necessary white metal.

FOAMING of the slag during the first stage of blowing is the result of not pouring off slag at the correct time; white metal becomes oxidized, and the  $\text{Cu}_2\text{O}$  formed reacts upon  $\text{Cu}_2\text{S}$ ; this sometimes takes place with sufficient rapidity to cause explosions. Skimming the slag frequently remedies the difficulty. According to McKenzie,<sup>2</sup> foaming before the matte reaches the white-metal stage is due to the surface of the matte sinking below the tuyère level when the air will blow direct into the slag. Foaming during the blister-forming stage, when little slag is made, occurs only rarely; the remedy is to charge some coal in order to reduce  $\text{Cu}_2\text{O}$ .

OVERBLOWING is an occasional accident, which is accompanied by the cooling of the copper. The ordinary treatment of such a case<sup>3</sup> consists in pouring into the converter small amounts of matte, from 10 to 15 lb., at a time, righting the converter after every addition until the enormous volume of  $\text{SO}_2$  suddenly set free has had time to escape; continuing with additions until  $\text{SO}_2$  ceases to be evolved; and finally adding enough matte to make up for the heat lost by the endothermic reaction of  $\text{Cu}_2\text{S}$  upon  $\text{Cu}_2\text{O}$  and by radiation. This final addition is about equal to the sum of the several additions necessary to reduce the  $\text{Cu}_2\text{O}$ .

In order to increase the life of the lining, feeding siliceous ore has been attempted in different ways. Blowing it in through the tuyère has always proved a failure;<sup>4</sup> the probable reason is that the  $\text{SiO}_2$  being cold does not combine with the FeO but floats to the surface and becomes entangled with the slag. Replacing sand by dried concentrates<sup>5</sup> did not prove sufficiently successful to adopt the procedure in regular practice. It will be shown later that with a large

<sup>1</sup>Brandt, *Metallurgie*, 1905, II, 311, 331.

Hesse, *op. cit.* 1906, III, 287, 375.

<sup>2</sup>*Eng. Min. J.*, 1910, XC, 750.

<sup>3</sup>McKenzie, *op. cit.*, 1910, XC, 1147.

<sup>4</sup>Wheeler-Krejci, *Tr. A. I. M. E.*, 1913, XLVI, 503.

<sup>5</sup>Wheeler-Krejci, *loc. cit.*

body of matte, as in the basic converter, in which the  $\text{SiO}_2$  can be brought to the right temperature, blowing in through the tuyères gives a different result.

A method of introducing  $\text{SiO}_2$  or siliceous ore into the acid converter, first practised at Great Falls, is to charge it after pouring the copper, spread it evenly, pour in some matte, allow this to stand for 2 or 3 min. in order to cement the ore to the lining, add the rest of the matte-charge, start the blast, and right the converter. The siliceous ore is brought gradually to the conversion temperature and slowly slagged. Thus at Anaconda 1000 lb. of ore was shot into the converter from a scoop (boat), and as many as 5000 lb. at Great Falls, as long as the acid converters were in operation.

**168. Elimination of Impurities.**—This important subject has been studied by Keller,<sup>1</sup> Douglas,<sup>2</sup> Van Liew,<sup>3</sup> Gibb,<sup>4</sup> Mathewson,<sup>5</sup> and Browne.<sup>6</sup> Keller gives the data assembled in Table 70 as the average elimination of impurity in converting.

TABLE 70.—ELIMINATION OF IMPURITIES IN CONVERTING

Element	S	Fe	Zn	Co	Ni	Pb	Bi	Sb	As	Te	Se
Per cent. elimination. . . . .	99	99	99	99	37	96	97	71	81	40	47

The curve of Mathewson, Fig. 358, gives the speed of elimination of Fe, S, and As in converting in the acid barrel converter, 8 ft.  $\times$  12 ft. 6 in., at Anaconda. For plotting, the percentage of Cu in the samples was chosen as the basis. The curves show that at the beginning of the blow during the first 10 min., S is more quickly oxidized than Fe, but that later the reverse is the case, until at 90 min. 98 per cent. of the Fe has entered the slag, when only 75 per cent. of the S has been changed into  $\text{SO}_2$ . The oxidation of Fe progresses slowly and evenly; that of S at a uniform rate up to 110 min., when  $\text{Cu}_2\text{S}$  is oxidized and  $\text{Cu}_2\text{O}$  reacts upon undecomposed  $\text{Cu}_2\text{S}$  causing  $\text{SO}_2$  to be emitted freely. The expulsion of As is very rapid during the first 10 min., and then progresses at a uniform slow rate. Gibb<sup>7</sup> points out that as regards the degree of elimination of impurities, such as As, Sb, and Bi, there is not much difference between converting and roast-smelting, but of course as regards speed there is no comparison. Losses in precious metals are taken up in § 770.

As to the composition of converter gases, Sticht<sup>8</sup> has found that during the slag-forming stage practically all the O of the blast is utilized. The percentage of  $\text{SO}_2$  in the gases rises, during the first 10 min., quickly from 1 to about 10 per cent. volume, and remains constant during the first stage; the free O present ranges from a trace to perhaps 1 per cent. volume. During the blister-forming

<sup>1</sup> *Tr. A. I. M. E.*, 1898, XXVIII, 146, 816; 1900, XXX, 310; *Min. Ind.*, 1900, IX, 257.

<sup>2</sup> *Tr. A. I. M. E.*, 1899, XXIX, 543.

<sup>3</sup> *Op. cit.*, 1904, XXXIV, 418, curves replotted by Gibb, p. 960.

<sup>4</sup> *Op. cit.*, 1903, XXXIII, 664.

<sup>5</sup> *Op. cit.*, 1907, XXXVIII, 154.

<sup>6</sup> *Op. cit.*, 1910, XLI, 296.

<sup>7</sup> *Tr. A. I. M. E.*, 1903, XXXIII, 664.

<sup>8</sup> Presidential Address, p. 44.

stage the content of  $\text{SO}_2$  rises quickly to about 18 per cent. volume, while free O appears to the extent of 0.5 per cent. and reaches 2 or 3 per cent. at the end of the blow. Hence the air-efficiency in the converter is high.

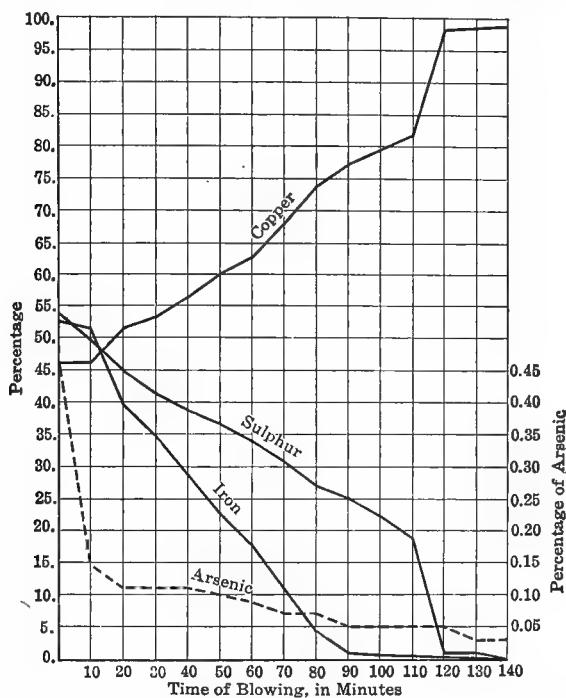


FIG. 358.—Speed of elimination of iron, sulphur, and arsenic in converting.

**169. Thermal Balances.**—The following calculation is based upon the records taken at Globe, Ariz., by Van Liew<sup>1</sup> and the considerations of Richards.<sup>2</sup> The chemical analyses of the samples taken during the blow are given in Table 71.

TABLE 71.—ANALYSES OF CONVERTER-SAMPLES

Sample	Cu	Fe	S	Zn	As	Sb	Ag	Au
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Original matte. . . . .	49.72	23.31	21.28	1.19	0.11	0.14	0.152	0.00055
Taken after 10 min. . . . .	50.20	23.15	20.95	1.20	0.09	0.12	0.147	0.00048
Taken after 20 min. . . . .	56.88	17.85	19.74	0.84	0.08	0.10	0.176	0.00069
Taken after 30 min. . . . .	64.60	10.50	18.83	0.70	0.08	0.13	0.191	0.00083
Taken after <sup>3</sup> 40 min. . . . .	76.37	2.40	16.30	0.45	0.08	0.13	0.240	0.00110
Taken after <sup>4</sup> 70 min. . . . .	99.120	0.038	0.159	0.090	0.0012	0.006	0.312	0.00111

<sup>1</sup> *Tr. A. I. M. E.*, 1904, XXXIV, 418.

<sup>2</sup> *Electrochem. Met. Ind.*, 1907, v, 356, "Metallurgical Calculations," McGraw-Hill Book Co., Inc., New York, 1908, p. 504.

<sup>3</sup> Last skim.

<sup>4</sup> Blister copper.

As the weight of the matte changes continuously during the blow, the chemical analyses can give no clear picture of the rate of elimination of the constituents. In order to obtain this, it is essential to find the weight of the matte at the end of each period, when the sample for chemical analysis was taken. During the slag-forming stage, *i.e.*, the first 40 min., very little Cu is oxidized; hence the error in assuming the weight of the Cu to remain constant is small. For the blister-forming stage, lasting 30 min., a loss of 1 per cent. Cu is assumed. If at the start, the Cu in 1000 kg. matte was 497.2 kg., the weight of the matte after 10 min. blowing was  $497.2 : 0.5020 = 990.4$  kg.; after 20 min.,  $497.2 : 0.5688 = 874.1$  kg.; after 30 min.,  $497.2 : 0.6460 = 769.7$  kg; after 40 min.,  $497.2 : 0.7637 = 651.0$  kg.; and lastly the weight of the blister copper after 70 min.,  $487.2 : 0.9912 = 491.5$  kg. By taking the weights at the end of each blowing period, by figuring the weights of the impurities from the analyses in Table 71, there are obtained the actual eliminations by deducting the total of the impurities, at one stage, from those at the preceding. Thus, 1000 kg. original matte contained 233.1 kg. Fe; after 10 min. blowing the weight of matte was reduced to 990.4 kg. with 23.15 per cent. = 229.3 kg. Fe; hence 3.1 kg. Fe were scorified. Table 72 is calculated in this manner.

TABLE 72.—WEIGHTS OF CONSTITUENTS AFTER EACH BLOWING PERIOD

Items	Cu	Fe	S	O <sup>1</sup>	Zn	As	Sb	Ag	Au	Total
	Kg.	Kg.	Kg.	Kg.	Kg.	Kg.	Kg.	Kg.	Kg.	Kg.
At Start	497.2	233.1	212.8	41.0	11.9	1.1	1.4	1.52	0.0055	1000.0
Eliminated in 1st period.....	0.0	3.8	5.3	0.1	0.0	0.2	0.2	0.06	0.0007	9.6
Weight at end of 10 min.....	497.2	229.3	207.5	40.9	11.9	0.9	1.2	1.46	0.0048	990.4
Eliminated in 2d period.....	0.0	73.3	35.0	2.9	4.6	0.2	0.3	-0.08 <sup>2</sup>	-0.0012 <sup>2</sup>	116.3
Weight at end of 20 min.....	497.2	156.0	172.5	38.0	7.3	0.7	0.9	1.54	0.0060	874.1
Eliminated in 3d period.....	0.0	75.2	27.6	-0.3	1.9	0.1	-0.1 <sup>2</sup>	0.07	-0.0004 <sup>2</sup>	104.4
Weight at end of 30 min.....	497.2	80.8	144.9	38.3	5.4	0.6	1.0	1.47	0.0064	769.7
Eliminated in 4th period.....	0.0	65.2	38.8	12.0	2.5	0.1	0.2	-0.09 <sup>2</sup>	-0.0008 <sup>2</sup>	118.7
Weight at end of 40 min.....	497.2	15.6	106.1	26.3	2.9	0.5	0.8	1.56	0.0072	651.0
Eliminated in 5th period.....	10.0	15.4	105.3	24.9	2.5	0.5	0.8	0.03	0.0617	159.5
Weight at end of 70 min.....	487.2	0.2	0.8	1.4	0.4	0.0	0.0	1.53	0.0055	491.5

In the thermal calculation, the heat evolved is found by taking the weight of each element oxidized, calculating the heat of oxidation and that of formation of slag, and then deducting the amount of heat expended in the dissociation of the equivalent amount of sulphide. The heat absorbed in breaking up the matte, *i.e.*, in separating the sulphides from one another, is not known, but is supposed to be small.

<sup>1</sup> By difference.

<sup>2</sup> The gains indicated are not actual, but are due either to inaccuracies of the assays or to a slight loss in the weight of Cu neglected in making out the table. In comparing the figures, it should be remembered that each of the first four periods lasted 10 min., while the fifth had a duration of 30 min.



FIRST PERIOD.—From start to end of 10 min.

Heat of oxidation:

Fe to $2\text{FeO} \cdot \text{SiO}_2$ , $3.8 \times 1,416 =$	5,381 Cal.
S to $\text{SO}_2$ , $5.3 \times 2,164 =$	1,146 Cal.
As to $\text{As}_2\text{O}_3$ , $0.2 \times 1,043 =$	209 Cal.
Sb to $\text{Sb}_2\text{O}_3$ , $0.2 \times 695 =$	134 Cal.
Total,	17,198 Cal.

Heat of dissociation of sulphides:

Fe from $\text{FeS}$ , $3.8 \times 429 =$	1,630 Cal.
As from $\text{As}_2\text{S}_3$ , $0.2 \times 2,000(?) =$	400 Cal.
Sb from $\text{Sb}_2\text{S}_3$ , $0.2 \times 1,433 =$	287 Cal.
Total,	2,317 Cal.

Net heat evolved during first period, 14,881 Cal.

In the manner indicated the Calories developed and absorbed by each element have been calculated severally for the different periods and assembled in Table 73. In it the heat units evolved have been collected in the Debit column, those absorbed by dissociation and carried away by the products in the Credit column; the difference between the two is given to loss by radiation, etc.

TABLE 73.—THERMAL BALANCE OF CONVERTER CHARGE

Debit, Cal.	Credit, Cal.
Fe to $(\text{FeO})_2 \text{SiO}_2$ :	Dissociation of $\text{FeS}$ :
Start to 10 min. .... 5,381	Start to 10 min. .... 1,630
10 min. to 20 min. .... 103,793	10 min. to 20 min. .... 31,446
20 min. to 30 min. .... 106,483	20 min. to 30 min. .... 32,261
30 min. to 40 min. .... 92,323	30 min. to 40 min. .... 27,961
40 min. to 70 min. .... 21,806	40 min. to 70 min. .... 6,607
S to $\text{SO}_2$ :	Dissociation of $\text{As}_2\text{S}_3$ :
Start to 10 min. .... 11,464	Start to 10 min. .... 400
10 min. to 20 min. .... 75,740	10 min. to 20 min. .... 400
20 min. to 30 min. .... 59,726	20 min. to 30 min. .... 200
30 min. to 40 min. .... 83,963	30 min. to 40 min. .... 200
40 min. to 70 min. .... 227,864	40 min. to 70 min. .... 100
As to $\text{As}_2\text{O}_3$ :	Dissociation of $\text{Sb}_2\text{S}_3$ :
Start to 10 min. .... 209	Start to 10 min. .... 287
10 min. to 20 min. .... 209	10 min. to 20 min. .... 430
20 min. to 30 min. .... 105	20 min. to 30 min. .... ..
30 min. to 40 min. .... 105	30 min. to 40 min. .... 287
40 min. to 70 min. .... 523	40 min. to 70 min. .... 1,148
Sb to $\text{Sb}_2\text{O}_3$ , total. .... 1,042	Dissociation of $\text{ZnS}$ :
Zn to $\text{ZnO}$ , total. .... 15,008	Start to 10 min. .... ..
4Cu to $(\text{Cu}_2\text{O})_2\text{SiO}_2$ . .... 4,323	10 min. to 20 min. .... 3,043
	20 min. to 30 min. .... 1,257
	30 min. to 40 min. .... 1,654
	40 min. to 70 min. .... 1,654
	Dissociation of $\text{Cu}_2\text{S}$ , total. .... 1,595
	Heat in 491.5 kg. Cu at $1200^\circ \text{C}.$ .... 85,945
	Heat in 424.0 kg. $\text{SO}_2$ at $1000^\circ \text{C}.$ .... 97,020
	Heat in 850.0 kg. N at $1000^\circ \text{C}.$ .... 226,741
	Heat in 526.0 kg. Slag at $1250^\circ \text{C}.$ .... 178,837
Total. .... 810,077	Total. .... 702,063
Matte at $1100^\circ \text{C}.$ , heat in original. .... 214,000	Loss by radiation. .... 322,014
Grand total. .... 1,024,077	Grand total. .... 1,024,077

The data of Table 73 rearranged to show the heats evolved during each period are given in Table 73a.

TABLE 73a.—HEATS EVOLVED IN THE SEVERAL BLOWING PERIODS

Item	Start to 10 min.	10 min. to 20 min.	20 min. to 30 min.	30 min. to 40 min.	40 min. to 70 min.	in 10-min period
	Cal.	Cal.	Cal.	Cal.	Cal.	Cal.
Heat of oxidation.....	17,198	185,954	168,793	179,793	258,339	86,113
Heat of dissociation.....	2,317	35,319	33,718	30,112	12,001	4,000
Net heat evolved.....	14,881	150,635	135,075	159,681	146,338	82,113

In Fig. 359 is given a graphical representation of the Calories evolved and absorbed in the preceding calculation, and of the net heat that remains available.

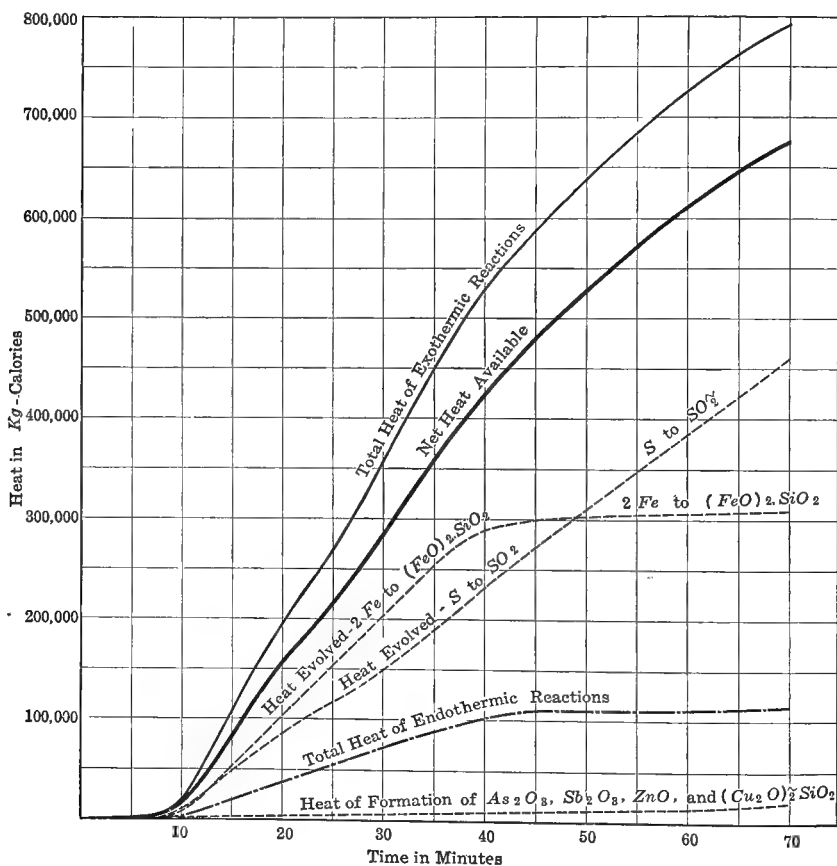
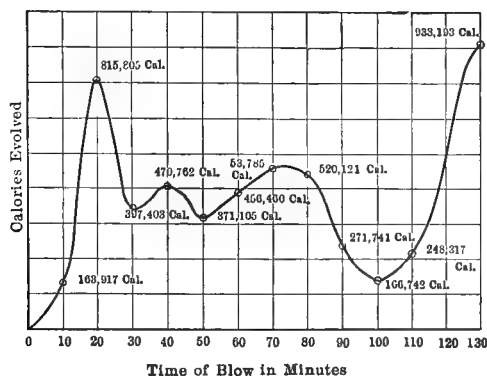
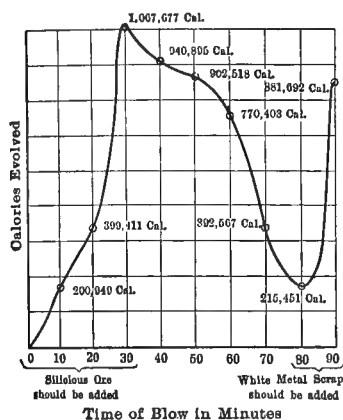


FIG. 359.—Graphical representation of thermal changes in converting.

In Figs. 360–361 are given two curves tracing the Calories evolved in blowing two acid charges at Anaconda in 1910. The results were obtained by a procedure similar to the one just given. Both curves show a quick rise of temperature at the beginning of the blow, a gradual fall during the second period,

and a sudden rise during the third. While the curve rises to the first and highest peak, siliceous ore may be added to the charge to keep down the temperature; when it reaches its lowest depression white metal may be added to furnish additional source of heat and prevent the temperature from becoming too low.



FIGS. 360-361.—Heats evolved in blowing acid converter-charges at Anaconda.

**170. Products, Losses, and Cost.**—The leading products of converting copper matte are blister copper, slag, flue-dust, and flue accretions; incidentally there have to be considered the slop and splash of the converters, and the shells and sculls of the converters and the ladles.

COPPER has a copper color; the surface of the ingot varies with the point to which the blow has been carried (p. 324).

TABLE 74.—ANALYSES OF CONVERTER COPPER

Element	Impure	Boston & Montana, normal	Boston & Montana, over-blown	Anaconda	Mont. Ore Purchasing Co.	Copper Queen		El Paso			
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Pb.....	0.055	0.0069	0.0016	0.0103	0.0517	0.084	0.103	0.07	0.16	0.16	0.41
Bi.....	0.057	0.0029	0.0015	0.0040	0.0051	.....	.....	.....	.....	.....	.....
Sb.....	0.15	0.0546	0.0195	0.0130	0.0533	0.009	0.014	0.135	0.059	0.067	0.008
As.....	0.108	0.0156	0.0072	0.0211	0.0231	0.012	0.016	0.039	.....	trace	0.06
SeTe.....	0.027	0.0034	0.0033	0.0072	0.0078	0.043	0.045	.....	.....	.....	.....
S.....	0.112	.....	.....	.....	.....	0.244	0.403	1.5	0.26	0.26	0.30
Cu.....	98.841	99.9166	99.9669	99.9944	99.8590	98.64	98.90	99.1	98.8	98.6	98.30
Fe.....	.....	.....	.....	.....	.....	0.159	0.184	.....	.....	.....	.....
Ni.....	.....	.....	.....	.....	.....	0.04	0.033	.....	.....	.....	.....
Zn.....	.....	.....	.....	.....	.....	0.027	0.004	.....	.....	.....	.....
Insol.....	.....	.....	.....	.....	.....	0.196	.....	.....	.....	.....	.....
Ag.....	0.641	.....	.....	.....	.....	12.24 <sup>5</sup>	11.13 <sup>5</sup>	111.8 <sup>5</sup>	83.7 <sup>5</sup>	108.1 <sup>6</sup>	184.4 <sup>5</sup>
Au.....	0.001	.....	.....	.....	.....	0.24 <sup>5</sup>	0.25 <sup>5</sup>	0.63 <sup>5</sup>	0.43 <sup>5</sup>	0.37 <sup>5</sup>	0.84 <sup>6</sup>
Ref.....	1	2	2	2	2	3	3	6	6	6	6

<sup>1</sup> Keller, *Tr. A. I. M. E.*, 1897, XXVII, 108.

<sup>2</sup> Douglas, *op. cit.*, 1899, XXIX, 543.

<sup>3</sup> Ounces per ton.

<sup>4</sup> Keller, *op. cit.*, 1898, XXVIII, 150, 157.

<sup>5</sup> Includes Ag and Au.

<sup>6</sup> Private Notes, 1912.

TABLE 75.—RARE METALS IN BLISTER COPPER<sup>1</sup>  
(In 100 Tons Blister Copper)

Locality	Au, oz.	Ag, oz.	Pt, oz.	Pd, oz.	Se, lb.	Te, lb.	Bi, lb.	Ni, lb.
Garfield.....	298.0	3,480	0.342	1.183	56.0	5.54	6.1	40.0
Steptoe.....	169.0	550	1.016	4.402	110.1	none	0.33	64.0
Omaha.....	360.0	23,090	1.825	6.486	26.6	67.1	18.6	944.0
Mountain.....	1,418.0	10,990	1.320	0.607	36.0	3.3	27.3	11.5
Tacoma.....	2,187.0	8,710	0.710	3.327	42.0	none	5.7	770.0
Aguas Calientes.....	482.0	67,300	0.416	0.226	170.0	none	4.0	12.0
Cerro de Pasco.....	170.0	9,900	0.319	0.589	13.7	none	13.5	32.0
Mount Lyell.....	464.5	7,205	0.624	1.374	42.0	none	4.3	166.0

THE CONVERTER SLAG, forming with 45-per-cent. matte from 60 to 70 per cent of the weight of the matte, usually approaches in composition the silico-silicate. As it contains from 2 to 3 per cent. Cu and is more basic than the ore-slag, it is returned to the ore-smelting charge. In some cases it is disposed of by means of a slag-casting machine (§ 165) and goes as lump-ore to the blast-furnace charge; in others it has been found to be more profitable to pour it into the blast-furnace settler; again it has been poured into the reverberatory furnace in order to render more fluid the siliceous charge.

THE SKIMMING-SLAG, which usually runs very much higher in Cu (over 10 per cent.) than the converting slag, has to go back to the ore-smelting furnace. Analyses of converter slag are given in Table 76.

TABLE 76.—ANALYSES OF CONVERTER SLAG

Component	Mont. Ore Purchasing Co.	Anaconda	Great Falls		Copper Queen		Cananea
SiO <sub>2</sub> .....	29.97	35.70	30.0	29.8	33.46	32.57	26.8
FeO.....	58.40	55.83	55.2	57.8	63.48	65.35	58.3
MnO.....		0.22					
Al <sub>2</sub> O <sub>3</sub> .....	3.55	1.76	9.5	10.0			6.2
CaO.....	2.12		1.0	1.0			1.5
ZnO.....	2.36	0.86				0.51	
Cu.....	1.09	2.14	2.00	1.6	4.47	3.18	2.44
Ni.....					0.96	0.19	
Pb.....	1.245					2.25	
Bi.....	0.001						
Sb.....	0.087						
As.....	0.021						
S <sub>2</sub> , Te.....	0.000						
S.....	0.250	1.03					
Ref.....	2	3	4	4		5	6

FLUE-DUST, of which less than 1 per cent. of the weight of the matte is formed, may run high or low in Cu depending upon where it settled. Material of Anaconda<sup>7</sup> collected near the hood averages Cu 71.23 and S 12.5 per cent.; a lower-

<sup>1</sup>Eilers, A. *Tr. A. I. M. E.*, 1913, XLVII.

<sup>2</sup>Keller, *Tr. A. I. M. E.*, 1898, XXVIII, 153.

<sup>3</sup>Private Notes.

<sup>4</sup>Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 307.

<sup>5</sup>Douglas, *op. cit.*, 1899, XXIX, 543.

<sup>6</sup>De Kalb, *Min. Sc. Press*, 1910, CI, 9.

<sup>7</sup>Offerhaus, *Eng. Min. J.*, 1908, LXXXVI, 751.

grade material collected farther away at Great Falls<sup>1</sup> assayed Cu 63.4, SiO<sub>2</sub> 3.8, FeO 12.8, S 16.0 per cent., Ag-Au 53.8 oz.; and Cu 37.8, SiO<sub>2</sub> 1.5, FeO 12.8, S 14.3, As 4.8 per cent. The following two more complete analyses of dust from the Montana Ore Purchasing Co., taken near and far from the converter, are by Keller:<sup>2</sup> Cu 23.32, Fe 3.30, Zn 2.85, Pb 18.81, Bi 0.42, Sb 0.935, As 1.805, SeTe 0.0026, S 1.34, SO<sub>4</sub> 34.46, H<sub>2</sub>O 10.87 per cent., Ag 18.2 oz; and Cu 2.36, Fe 2.80, Zn 5.53, Pb 32.24, Bi 0.48, Sb 2.186, As 5.694, SeTe 0.0054, S 0.0, SO<sub>4</sub> 36.15 per cent., Ag 6.4 oz. An analysis of the gas passing through a converter flue gave Dunn<sup>3</sup> SO<sub>2</sub> 2.845, SO<sub>3</sub> 0.0515, CO<sub>2</sub> 0.2084, H<sub>2</sub>O 1.061, As<sub>2</sub>O<sub>3</sub> 0.00073, O 12.04, N 83.64 per cent. volume.

THE LOSS in Cu and Ag-Au<sup>4</sup> has been variously estimated; so far no accurate determinations have been made excepting perhaps those of Mount Lyell, where the loss of Cu is 2.02 per cent., of which 1.17 per cent. is incurred in converting and 0.85 in retreating intermediary products; and that of Ag 1.18 per cent. of which 0.68 per cent. is due to converting. It is generally held that with a matte free from or low in volatile metals such as Pb and Zn, and with suitable dust-chambers, the loss of Cu in converting does not exceed 1.5 per cent.; the loss of Ag is about 2.5 per cent., and the loss in Au is *nil*. The presence of lead greatly increases the loss as shown by the recent figures of Moore,<sup>5</sup> and Semple,<sup>6</sup> but here also the loss in Ag rises and falls with that of the Cu in the fume. With the present possibility of filtering converter gases, this disputed question ought to be near its decision.<sup>7</sup> There is full agreement in the opinion that the loss during the slag-forming stage is negligible, and that it becomes apparent only during the blister-forming stage. The danger of drawing conclusions from laboratory experiments upon this question of loss in converting is evidenced by Günther<sup>8</sup> who found, in treating, in a small barrel converter, matte from Mansfeld with Zn 3.7-7.4 per cent., losses which exceeded the entire loss of the complete treatment from raw ore to blister copper.

THE COST of converting 40-per-cent. matte in the Central West is given by Austin<sup>9</sup> as \$4.83 per ton of matte. According to Moore,<sup>10</sup> the cost per ton of blister copper varies from \$4.53 to \$9.76 as seen in Table 78. The Tennessee Copper Co. converts<sup>11</sup> in a basic vessel at a cost of 0.709 cents per pound fine copper; the Mammoth Copper Mining Co.<sup>12</sup> at a cost of 0.75 cents starting with matte of 15-20 per cent. Cu.

<sup>1</sup> Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 30.

<sup>2</sup> *Tr. A. I. M. E.*, 1898, XXVIII, 154.

<sup>3</sup> *Tr. A. I. M. E.*, 1913, XLVI.

<sup>4</sup> Sticht, Presidential Address. Summary.

<sup>5</sup> *Eng. Min. J.*, 1910, XC, 263; *Tr. A. I. M. E.*, 1913, XLVI.

<sup>6</sup> *Eng. Min. J.*, 1911, XCI, 508.

<sup>7</sup> Ricketts, Loss at Cananea, *Eng. Min. J.*, 1911, XLI, 1246.

<sup>8</sup> *Metallurgie*, 1905, II, 539.

<sup>9</sup> *Min. Sc. Press*, 1911, CII, 178.

<sup>10</sup> *Eng. Min. J.*, 1910, XC, 464.

<sup>11</sup> *Eng. Min. J.*, 1912, XCIII, 1034.

<sup>12</sup> *Op. cit.*, 1912, XCIV, 982.

TABLE 78.—COST OF CONVERTING PER TON OF BLISTER COPPER

Plant	Matte, Cu per cent.	Cost, \$	Matte, Cu per cent.	Cost, \$	Matte, Cu per cent.	Cost, \$	Matte, Cu per cent.	Cost, \$
A.....	38.2	8.40	37.0	8.55	41.1	7.73	41.1	5.76 <sup>1</sup>
B.....	42.8	8.50	.....	.....	.....	.....	.....	.....
C.....	41.9	9.00	.....	.....	.....	.....	.....	.....
D.....	43.5	4.53	42.7	4.92	41.6	5.30	.....	.....
E <sup>2</sup> .....	40.2	4.47	.....	.....	.....	.....	.....	.....

## b. CONVERTING IN VESSEL WITH BASIC LINING

**171. Basic Converting in General.**—The necessity for frequent renewal of the lining in the ordinary acid converter has been the cause of experiments with a lining which is not attacked chemically by the process. The best lining so far has been one of magnesite brick; and this has given the new apparatus the name of Basic Converter, although the basic character of the lining has nothing to do with the process, because it remains unchanged. The  $\text{SiO}_2$  necessary for slagging the  $\text{FeO}$  is supplied by the siliceous ore charged. The early working tests with a really basic process by Keller<sup>3</sup> and Westinghouse (p. 300), as well as the laboratory experiments by Schreyer<sup>4</sup> and Styri<sup>5</sup> have proved the futility of trying to work without  $\text{SiO}_2$ . Pyritic smelting in a converter lined with magnesite by Knudsen (p. 196) and the partially successful work of Baggaley<sup>6</sup> have already been described.

The use of an inactive lining in the form of magnesite brick in a barrel-shaped vessel for converting copper matte, with the addition of  $\text{SiO}_2$  to slag the  $\text{FeO}$  formed, has been carried to a successful end by W. H. Peirce and E. A. C. Smith at the works of the Baltimore Copper Smelting and Rolling Co., and the result is the "Peirce-Smith Basic Converter," which is the outcome of work extending over several years.<sup>7</sup> The process has been so eminently successful that it is replacing acid converting in most smelteries and will continue to do this unless it meets special conditions, such as occur in localities where a high smelting charge can be obtained for siliceous ore better suited for a lining than for charging into the converter, which make it more profitable to use an acid lining.

The main advantages of the basic over the acid converter are:<sup>8</sup> the decreased cost of lining (one basic lining for 2500 tons of Cu vs. one acid for 10 tons); the greater air-efficiency (75 vs. 60 per cent.), on account of the use of a metal tuyère-

<sup>1</sup> Basic converter.<sup>2</sup> Lead-copper matte.<sup>3</sup> P. 299, and *Tr. A. I. M. E.*, 1913, XLVI, 474.<sup>4</sup> *Metallurgie*, 1909, VI, 190.<sup>5</sup> *Op. cit.*, 1912, IX, 426, 449.<sup>6</sup> P. 300, *Tr. A. I. M. E.*, 1913, XLVI, 480.<sup>7</sup> Editor, *Eng. Min. J.*, 1911, XCI, 944.<sup>8</sup> Moore, *Eng. Min. J.*, 1910, XXXIX, 319;Mathewson, *Tr. A. I. M. E.*, 1913, XLVI, 473.

pipe; the use of larger vessels (40 tons Cu *vs.* 20 tons), accompanied by economies in labor, power (one-half), and repairs; the use of low-grade matte and of siliceous ore with  $\text{SiO}_2$  35+ per cent.; the small amount of intermediary product to be retreated (per ton Cu: 1.6 tons of slag with 1.5 per cent. Cu *vs.* 2.4 tons with 6 per cent.), and the consequent large direct output of blister copper (95 *vs.* 70); the formation of basic slag to serve as flux in the blast-furnace; the neatness and cleanliness of plant; and the decrease in danger from accident and dust.

The disadvantages are: blowing out of fines; time required for repairing and lining; care in manipulation; continual punching of tuyères.

Shortly after the Peirce-Smith converter had proved to be a success at Garfield (early in 1910), the Anaconda Company lined its horizontal converters with magnesite and proved that success was not confined to the details of the Peirce-Smith vessel; the same was done at Great Falls (first attempt 1897, second 1901, chrome brick 1906, use of magnesite 1911) with the upright converter. In fact, the work with this upright 12-ft. vessel lined with magnesite brick has been so advantageous that in new basic installations<sup>1</sup> such as Copper Queen, Cananea, Calumet & Arizona, Arizona Copper Co., Mason Valley, and others, the upright converter is preferred to the horizontal. The Great Falls converters, after having been in operation for two years, had their original lining, when put out of commission to make way for the 20-ft. converters now in operation.

Basic converting will be discussed in connection with the three forms of converters which have become typical for the present practice: the Peirce-Smith, the Anaconda, and the Great Falls.

**172. The Peirce-Smith Converter.**<sup>2</sup>—The converter manipulated with electric power is shown in Figs. 362–365; the hydraulic manipulation is represented by Fig. 366. The converter is a horizontal cylindrical shell, *a*, of  $\frac{5}{8}$ -in. steel plate; it usually is 26 ft. long, 10 ft. in diameter, and holds 30 tons of copper; the shell is open at the top for 4 or 5 ft. to allow for expansion of the lining, and is tied by rods, *b*. Some converters recently installed are 36 ft. long (Steptoe, Copper Cliff), 10 ft. in diameter, and hold from 50 to 60 tons of copper. The arch of the lining rises slowly but steadily while the converter is running, and in time breaks down. The pair rests on and revolves with three cast-steel I-beams, *c*, riveted to it, on three pairs of carrying rollers, *dd'*. The base of the front roller, *d*, of each pair is fixed, while that at the back carries on trunnions two smaller rollers, *d'*, in order that the weight of the converter, over 175 tons when filled, may be evenly distributed. The flat heads, *e*, also of  $\frac{5}{8}$ -in. steel, are made adjustable in order that they may yield to the longitudinal thrust of the expanding lining. This is accomplished by a riveted flange which extends telescopically into the cylindrical shell. A head is held in place by I-beams

<sup>1</sup> Editor, *Eng. Min. J.*, 1913, xcv, 335.

<sup>2</sup> Vail, *Eng. Min. J.*, 1910, lxxxix, 563.

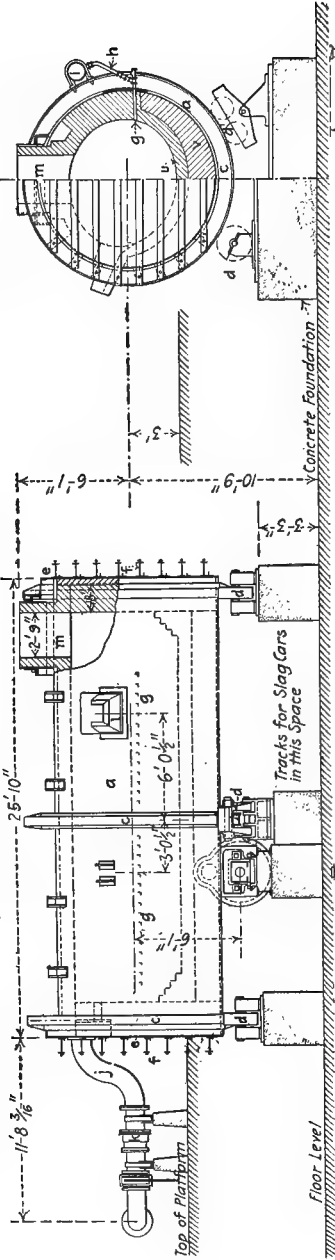
Moore, *op. cit.*, 1910, lxxxix, 1317; *A. I. M. E. Bull.* 83, Nov., 1913.

Neel, *Eng. Min. J.*, 1911, xci, 707, 964.

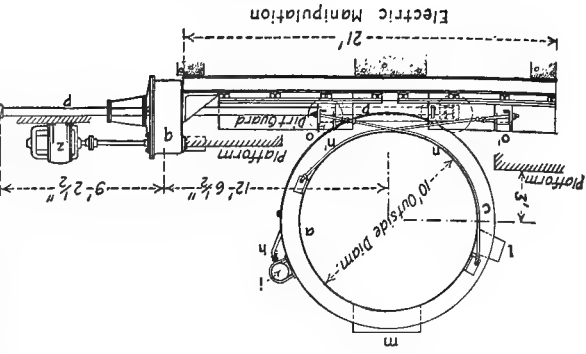
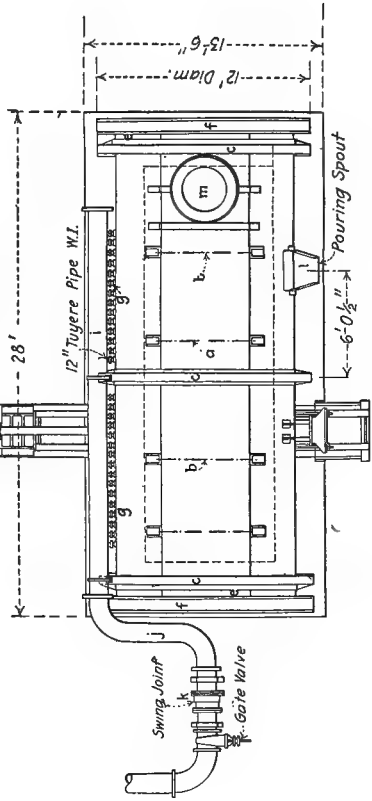
Hamilton, *A. I. M. E., Bull.* 83, Nov. 1913.

Editor, *Eng. Min. J.*, 1914, xcvi, 720.

End Elevation      Cross-Section



Plan





which are spaced over the outer surface and connected with the nearest cast-steel I-beam friction-ring by tie-bolts provided with nuts. A bolt passes through the ring and a piece of flat-iron bearing on the flanges of the cast beam. Loosening the nuts, when the furnace is being heated, furnishes the necessary expansion space. The strain on a bolt is indicated by the bending of the flat-iron.

On the blowing-side a short distance beneath the median horizontal plane are 32 cast-iron tuyères, 2 in. square with 1.25-in. holes, extending through the lining and pitching downward, which are provided with improved Dyblie valves and severally connected by a flexible hose, *h*, to the wrought-iron blast-pipe, *i*.

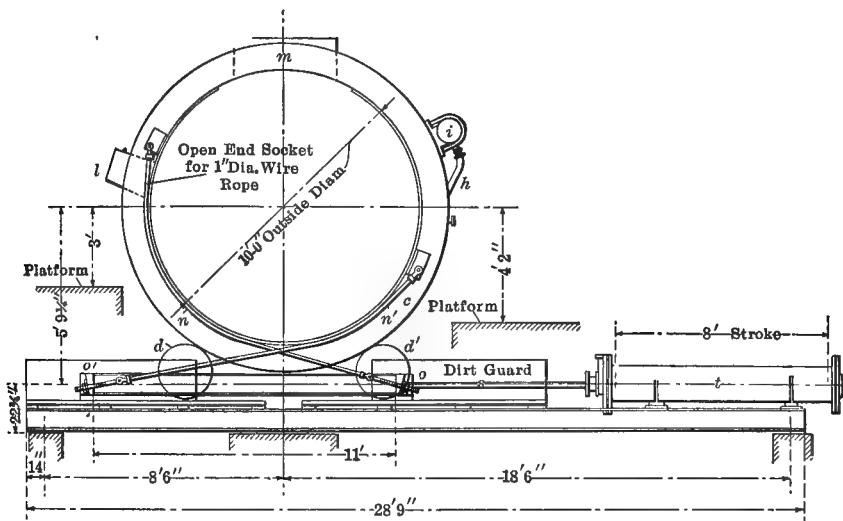


FIG. 366.—Hydraulic manipulation of Peirce-Smith converter.

This is bolted to the converter shell and connected by a cast-iron pipe, *j*, and a swing-joint, *k*, with the stationary blast-main leading to the blowing-engine. Sometimes tuyères are omitted opposite the discharge spout in order to diminish the loss by splashing. Along the tuyère line the shell contains movable plates to allow repairing the 18-in. tuyère-belt from the outside without cooling the converter.<sup>1</sup> At some plants the cast-iron tuyère has been replaced by a wrought-iron pipe, which works equally well and makes replacement more convenient.

In a converter 26 ft. in length the number of tuyères may not fall below 20, as the heat generated becomes insufficient; with the throat of the converter placed at the center instead of at the side (see below), the number of tuyères has been increased to 37, with the result that converting proceeded 27 per cent. more quickly than with 32 tuyères.

<sup>1</sup> Detail, see *Eng. Min. J.*, 1913, xcv, 322. This arrangement is of more importance when lead-bearing matte (Cu 40, Pb 15-18) is treated than with regular copper matte.

On the pouring side, *i.e.*, the breast, is an opening with spout, *l*, for the removal of slag and blister copper. It is closed with magnesite brick and clay. For pouring off slag, an opening, about 3 in. in diameter, is made in the upper or clay part of the breast; for casting the copper, the tap-hole in the lower part is opened. In pouring the copper, the magnesite breast acts as a skimmer by holding back the slag which remains in the vessel. Some vessels have separate openings for matte and copper.

In one end of the converter is an opening, not shown, for the insertion of an oil-burner to heat up the furnace, either at the start or in case the copper cools too much on account of delay or some other cause.

On the top and at one end of the vessel is the throat, *m*, which receives matte and siliceous ore, and delivers the gases to the flue leading to the dust-chamber. The sheet- or cast-iron throat is lined with magnesite if the flame tends to burn out the lining; with clay if there is a tendency to form accretions, as is especially the case with Pb-Cu matte.<sup>1</sup> As stated above, the throat has been transferred to the center at some plants. This has been found advantageous for the even spreading of the siliceous ore; dried concentrates move more easily than does ore.

The manipulation is effected by two wire ropes, *n n'*, of which one end is attached to the converter, the other to a block, *o o'*, sliding in guides. The blocks are firmly connected with a threaded hollow shaft, *p*, and this is rotated by a threaded gear which in the casing, *q*, engages a pinion direct-connected with the shaft of the dynamo, *r*. The hydraulic manipulation is shown in Fig. 366. Here the blocks, in which the wire ropes are anchored, are direct-connected with the piston-rod, *s*, of the hydraulic cylinder, *t*.

The working lining is made of 9-in. magnesite brick excepting at the tuyère-belt, where 18-in. magnesite slabs extend 8 in. below and 24 in. above the tuyères. The bottom is protected with fire-brick, *v*, 13 in. thick along the center, tapering to about 4 in. on the sides and reaching 8 in. below the tuyère level. In a 26-ft. vessel the dimensions of the oval cavity are: length 20 ft., width 7 ft. The magnesite brick are laid in dry magnesite powder except in the tuyère-belt where a mixture of magnesite powder and linseed oil is used. In order to furnish space for expansion,  $\frac{1}{4}$ -in pine liners are placed after every eighth course of 9-in. brick. In many works, the tuyère-region is packed 8 in. above and below the tuyères with a ground mixture of calcined magnesite and asbestos with 5 per cent. silicate of soda, first used at Anaconda by Mathewson. This mixture appears to work most satisfactorily, but requires careful warming in order to prevent spalling. A lining of chrome brick or some other non-corrosive material has been suggested to replace magnesite.

The 26-ft. converter in working order weighs from 125 to 135 tons; with the charge, this weight is increased to 165-175 tons. The blast-pressure ordinarily does not exceed 11 lb. per square inch, and the volume ranges from 90,000 to 100,000 cu. ft. of air at sea-level per ton of blister copper starting with 40-per cent. matte. The air-efficiency is about 75 per cent. and reaches 90 per-cent.

<sup>1</sup> Howard, L. O. "Collar-puller for Converters," *Min. Sc. Press*, 1913, CV1, 733.

Accessories are similar to those of the acid converter and the arrangement of plant shows little difference.

In starting, the converter is brought to the required temperature by a wood fire (18 hr.), followed by an oil-burner (8 hr.) introduced at one end, or by heating with coke (6 hr.). When hot, an initial bath of matte, 30 to 40 tons with a 26-ft. vessel, is poured in through the throat and followed by from 6000 to 7000 lb. dried siliceous ore shot in, from a boat or a rectangular box of sheet iron contracted at one end to a pouring spout and suspended from a crane. Blast, of about 5 lb. pressure, is turned on for 2 or 3 min., and the converter turned over until the tuyères are well covered by the matte. The ore spreads out over the surface of the matte. When evenly distributed, the vessel is turned over an additional amount, and the volume of air increased to from 6000 to 8000 cu. ft. per min.; this gives a pressure of 10 to 12 lb. with the tuyères immersed 24 in. below the surface of the bath. Blowing "on matte" 30 to 45, and sometimes 60 min., will cause the  $\text{FeO}$  and the gangue of the siliceous ore to form a thin slag which can be poured off readily. The fluidity of the slag is tested with an iron rod. The slag is poured off, and from 8 to 10 tons of liquid matte poured in from one ladle, or perhaps 13 tons from two ladles. The vessel is brought to its central position, *i.e.*, one in which the tuyères are not immersed and the slag is not flowing, and a tubful of siliceous ore (5000 to 6000 lb.) added. After this, the vessel is again turned over on the tuyères, and converting continued for about 30 min. This cycle of operations is repeated with decreasing charges a sufficient number of times (usually for 7 hr.) to obtain the requisite amount of white metal, about 60 tons, to furnish 42 to 48 tons of blister copper; the white-metal bath will reach within 2 to 4 in. of the tuyère-level. It is essential that in the several pourings of slag, only little slag be left floating on the matte, as this retards oxidation. The critical stage of the entire converting lies in slagging off the last iron before the white-metal stage; an excess of  $\text{SiO}_2$  makes the slag sticky and a lack causes  $\text{Fe}_3\text{O}_4$  to be formed. The white metal is now blown in the usual way in about 4 hr. to blister copper. At the end of the blow a small amount of rich slag is formed, which is taken care of by the next charge. Thus blowing on matte for about 7 hr. and on copper for about 4 hr. gives one pour of blister copper.

The grade of matte usually blown is the same as in the acid converter, *viz.*, Cu 45 per cent. Matte of lower grade, say Cu 30 per cent., is worked in the same manner; only it takes a longer time to fill the converter with white metal.

**THE ORE-CHARGE.**—The siliceous ore charged may vary greatly in composition and size; the conditions to be fulfilled are that there shall be an excess- $\text{SiO}_2$ , and that the other components shall not cause the slag to be sticky. A content of  $\text{SiO}_2$  35 per cent. forms a low figure; however, the Utah Copper Co. concentrates with  $\text{SiO}_2$  28, Fe 12,  $\text{Al}_2\text{O}_3$  1, Cu 26, are used regularly as flux; the amount that can be used is limited, as the material tends to fill the converter. A few partial analyses of siliceous ores charged are given in Table 79.

TABLE 79.—ANALYSES OF SILICEOUS ORES CHARGED WITH BASIC CONVERTER

Element	El Paso	El Paso	Cananea	Garfield	Steptoe
Cu.....	6.8	6.6	.....	1.2	4.32
Pb.....	none	none	.....	.....	.....
Insol.....	78.8	76.3	.....	.....	.....
SiO <sub>2</sub> .....	.....	70.1	82.0	76.0	66.0
Fe.....	5.1	6.6	3.4	7.0	4.82
Mn.....	none	none	.....	.....	.....
CaO.....	1.1	trace	1.0	.....	0.69
MgO.....	.....	.....	.....	.....	.....
Al <sub>2</sub> O <sub>3</sub> .....	.....	.....	8.0	.....	9.95
Zn.....	none	none	.....	.....	.....
S.....	3.4	trace	.....	3.0	3.83
Size.....	.....	.....	.....	$\frac{1}{2}$ in.	.....
Ag oz. per ton...	2.4	.....	.....	.....	.....
Au oz. per ton...	0.05	.....	.....	.....	.....

As to size, the ore is usually not coarser than  $\frac{5}{8}$  in.; ore crushed through a 4-in. ring makes sufficient fines to allow the whole to be used without further comminuting. Very fine concentrates are blown into the vessel through one or more tuyères by means of the Day apparatus, which is shown in Fig. 373. The flux, of course, has to be approximately dry, *i.e.*, it may not retain more than 4 or 5 per cent. H<sub>2</sub>O. The Mac Dougall furnace (§ 64) heated from a small coal fire or an oil-burner serves this purpose effectively; a rotary dryer 3 ft. in diameter, 30 ft. long, will handle 40 tons of material in 10 hr., with two men, at a cost of \$0.10 per ton.

THE TUYÈRES have to be punched consecutively during the entire blow. Two and sometimes three men per shift are necessary for this work. The tuyère-pipe has a removable cap which contains an opening for this purpose. During stops the cap is taken off and the entire face of the tuyère cleaned. Two sets of punching bars are used, each of  $\frac{3}{4}$ -in. steel about 4 ft. long; the ordinary tool has a punching-head 1 in. in diameter and a hammer-head  $2\frac{1}{4}$ -in.; the cleaning tool, used when the converter has been turned down to be emptied, has a punching-head  $1\frac{1}{8}$  in. in diameter, and a  $2\frac{1}{4}$ -in. hammer-head.

The slag, as stated above, has to be thin in order to pour well. The SiO<sub>2</sub>-content may range from 20 to 30 per cent.; with clean copper matte it varies from 25 to 27 per cent.; with leady matte it is as low as 23 per cent. If the SiO<sub>2</sub> goes below 20 per cent., Fe<sub>3</sub>O<sub>4</sub> forms and incrusts the bottom. The additions of flux have to be carefully regulated. At Garfield the maximum capacity of vessel of 65 tons blister copper was reduced in the early stages of converting to 25 tons by Fe<sub>3</sub>O<sub>4</sub> building along the bottom. It was once held that, if the SiO<sub>2</sub>-content was higher than 30 per cent., it attacked the magnesite lining. This belief has been proved to be erroneous by Mathewson<sup>1</sup> who by the analyses given in Table 80 shows that there is no connection between SiO<sub>2</sub>- and MgO-contents of a slag.

<sup>1</sup>Tr. A. I. M. E., 1913, XLVI, 473.

TABLE 80.—CONTENT OF MgO AND SiO<sub>2</sub> IN SLAGS OF BASIC CONVERTER

Cu	SiO <sub>2</sub>	FeO	CaO	MgO
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
2.2	37.8	46.3	1.1	0.6
2.2	37.2	46.6	1.0	0.6
3.80	35.1	48.3	1.0	0.6
2.80	34.5	49.3	1.0	0.6
3.20	33.5	50.3	1.0	0.5
3.80	31.6	51.4	1.4	0.5
1.80	30.8	52.5	1.3	0.8
2.20	28.9	56.0	1.0	0.5
2.40	28.0	56.5	0.9	0.5
3.00	25.8	56.6	1.0	0.5
4.60	24.6	56.2	1.0	0.7
4.60	22.4	58.3	1.3	0.7
4.20	23.4	58.1	1.1	0.4

In blowing, the fluidity of the slag is tested by inserting a bent rod through the slag-pouring opening and quickly withdrawing. The rod ought to pass readily through the slag, and the coating on it when withdrawn ought to be smooth without showing any nobs. Another method of testing the fluidity is to pour some slag from the converter or a ladle onto a shovel and observe the flow. Foaming of slag occurs during the blister stage; it is attributed by Moore<sup>1</sup> to the charge being too cool; others attribute it to an excess of SiO<sub>2</sub> in the charge; Liddell<sup>2</sup> found in the early stages of the process at Baltimore, when the converter was heated in part as is a reverberatory furnace, that CO was evolved.

The temperature of the converter is lower than the temperature of the acid vessel; the slag formed is a subsilicate which has a lower formation temperature than the singulo-silicate; large quantities of ore are charged which cool the bath; and the solution of the constituents of the ore absorbs heat. A temperature exceeding 1150° C. retards the conversion, attacks the lining, and makes sticky tuyères; running the temperature too low prevents FeO from combining with SiO<sub>2</sub>, causes the formation of Fe<sub>3</sub>O<sub>4</sub>, and makes the punching of tuyères very hard. Temperatures of the different stages of a blow have been taken by Clevenger.<sup>3</sup>

The progress of a blow may be followed with clean matte, by watching the flame. It is brown at first, becoming greenish as the Cu-content increases; the greenish flame becomes paler showing pale blue streaks, and is about two-thirds pale blue when the matte has reached the white-metal stage. With leady or dirty mattes the color of the flame gives no indications of the progress made. Examination of the fracture of matte from cooled ladle-samples gives a good idea of the Cu-content. The approach to the white-metal stage is recognized by the behavior of the white metal on the rabble. In blowing for copper the flame becomes at first reddish-brown and later bronze.

<sup>1</sup> *Eng. Min. J.*, 1910, LXXXIX, 1319.

<sup>2</sup> *Eng. Min. J.*, 1910, XC, 104.

<sup>3</sup> *Met. Chem. Eng.*, 1913, XI, 448.

The end of a blow is determined by the appearance of the copper on a rod inserted into the bath and quickly withdrawn (finishing on the rod). The metal is rose color, full of pinholes and free from dark patches of undecomposed matte.

The time required for a blow with 40 tons of 45-per-cent. matte to furnish 45 tons blister copper is about 20 hr.; or a converter produces about 50 tons of blister copper per day from 40-per-cent. matte.

A campaign lasts about 100 charges of 40 tons of 45-per-cent. matte with a production of about 3000 tons of blister copper. It then becomes necessary to repair the lining surrounding the tuyères for a width of about 18 in. This takes six days, *i.e.*, three days for cooling sufficiently to allow a man to enter the vessel (quicker cooling causes the brick to spall), two days for repairing, and one day for heating up. Smaller repairs at the tuyère-belt, of a section at a time, which can be made from the outside and do not require cooling the vessel, take about two days. Repairs cost about \$0.25 per ton of blister copper. The rest of the lining lasts much longer than that of the tuyère-belt; thus the roof, which becomes coated with slag, lasts from two to three times as long, and the lining below the metal line is not attacked by the process; it may have to be replaced only on account of the accumulation of  $\text{Fe}_3\text{O}_4$ , which has to be broken out. Additions of spiegeleisen may assist in eating out the crust.

No facts have been recorded so far as to the elimination of impurities excepting that the expulsion of As goes on as long as there is S present in the charge. The rate and amount of expulsion ought to be about the same as in the acid process.

**173. Products, Losses, and Cost.**—The main products are blister copper, slag, and flue-dust.

THE BLISTER COPPER is practically the same as in the acid process; analyses have been given in Table 74. It is sometimes poured from the converter into a barrel-shaped oil-heated receiver, resting on a car, and delivered from this to a casting machine. Typical examples are El Paso and Hayden.

The slag analyses given in Table 81 show the general character of the product.

TABLE 81.—ANALYSES OF CONVERTER SLAG

Locality	SiO <sub>2</sub>	Fe	Mn	CaO	Al <sub>2</sub> O <sub>3</sub>	Cu	S	Zn	Ag, oz.	Reference
Perth Amboy.....	26.6	43.2	.....	.....	.....	1.6	.....	.....	.....	Moore, <i>Eng. Min. J.</i> , 1910, LXXXIX, 1319.
Garfield.....	27.5	47.4	.....	.....	.....	1.73	0.9	.....	.....	Neel, <i>op. cit.</i> , 1911, xci, 964.
El Paso. ....	23.4	45.1	1.0	1.0	3.6	3.1	1.2	2.7	2.7	Private Notes.
Cananea.....	25.0	44.0	.....	1.0	3.0	.....	1.0	.....	.....	Private Notes.
Garfield.....	30-31	46-47	.....	.....	.....	1.1	1.5	.....	.....	Private Notes.
Steptoe.....	22.8	49.4	.....	0.3	4.7	2.18	.....	1.0	.....	Private Notes.
Steptoe.....	23.6	48.0	.....	0.3	4.8	2.25	.....	1.5	.....	Private Notes.

**FLUE-DUST.**—The amount of flue-dust formed varies of course greatly with the character and size of the siliceous ore charged; it is about 3 per cent. It has been found that with the throat of the converter at the center instead of at the side, the distribution of siliceous ore is more even and thereby the loss in flue-dust about one-half.

TABLE 82.—ANALYSES OF FLUE-DUST FROM BASIC CONVERTER

Locality	SiO <sub>2</sub>	Fe	Mn	CaO	Al <sub>2</sub> O <sub>3</sub>	Cu	S	Zn	Pb	Ag, Au, oz.	Reference
El Paso.....	16.3	8.6	trace	1.6	.....	45.4	10.9	4.8	12.0	49.56	Private Notes.
Cananea.....	6.7	15.0	.....	1.1	2.0	50.7	13.3	.....	.....	19.08	Private Notes.

At the Garfield smelter an experimental Cottrell electric condensation plant<sup>1</sup> is in successful operation treating the fume and dust from one Peirce-Smith converter.

The collecting-electrodes are vertical wrought-iron pipes, 10 ft. long and 5 in. in diameter, standing on a floor; in the centers are suspended discharge wire-electrodes. The condensation-flue contains 608 pipes and receives through natural draft 40,000–50,000 cu. ft. gas per min. An A. C. of 2300 volts is stepped up by a transformer to 23,000–30,000 volts, and changed by rectifiers, run by three-phase synchronous 220-volt motors, to a D. C. of the same voltage. The results have shown that 97.25 per cent. of the Pb in the gases is recovered; the collected material containing Pb 40, Cu 3, Insol, 3, Fe 4, As 7, Zn 2, S 9 per cent; Ag 6.0 and Au 0.05 oz. per ton. An installation for the treatment of the gases of the converting department is being erected.

**COPPER LOSS.**—The loss of Cu in the basic process is small, as the Cu-content of the slag is < 2 per cent.; in fact 95 per cent. of the Cu in the matte is recovered as blister copper *vs.* 65 per cent. in the acid converter.

**THE LABOR** on a shift consists of one skimmer and two helpers for punching tuyères.

**THE COST.**—The cost per ton of copper is inversely proportional to the Cu-content of the matte, *e.g.*, \$6.00 with 30-per-cent. *vs.* \$4.00 with 45-per-cent. matte; but considering that the Cu lost in the ore blast-furnace slag with 30-per-cent. matte is perhaps 0.25 per cent. and with 45-per-cent. matte 0.50 per cent., the balance may lie in favor of 30-per-cent. matte. The cost in Utah is about \$4.00 per ton of blister copper, including casting, sampling, and loading; with acid work it was about \$9.00.

**174. Concrete Examples.**—Three concrete examples may serve to further illustrate the work of the Peirce-Smith basic converter.

(1) **GARFIELD.**—The cylinder is 24 ft. long and 10 ft. in diameter outside dimensions, the central throat 3 ft. 4 in.; the shell of the cylinder is of  $\frac{1}{2}$ -in. steel plate, that of the hood of  $\frac{3}{8}$ -in. plate lined with 1-in. cast-iron plates; the lining at the bottom is 20–24 in. thick; at the tuyère belt 18–20 in.; opposite the tuyères 12 in.; at the hood on the tuyère-side 12 in. and opposite 9 in. There are 37 tuyères  $1\frac{1}{4}$  in. in diameter placed 18 in. above the bottom.

The first charge is 70,000–80,000 lb. matte and 8000 siliceous ore, subsequent charges are 12,000–15,000 lb. matte and 2000–8000 lb. siliceous ore. A single blow on matte lasts 20–30 min., one on white metal 4.5–5 hr.;

<sup>1</sup> Cottrell, *Tr. A. I. M. E.*, 1912, XLIII, 512, 755.

Hofman, "General Metallurgy," 1913, p. 858.

Howard, W. H., Private Communication, Dec., 1913.

the total blowing-time of a charge is 6 hr. on matte, 5 hr. on copper, or a total of 11 hr.; the operating time of a charge is about 16.5 hr. The blast-pressure is 10 lb.; the grade of matte, Cu 40 per cent.; the character of the siliceous ore:  $\text{SiO}_2$  76, Fe 7, Cu 1.2, S 3 per cent., its size  $2\frac{1}{2}$  in. The tons of Cu produced per lining average 4200, the maximum has been 6000 tons. The labor required is one skimmer and two punchers per shift.

(2) STEPTOE.—There are two Peirce-Smith converters, one 32 by 10 ft., the other 24 by 10 ft. outside dimensions. The central throats are 42 and 38 in. in diameter; the lining is 13–18 in. thick; there are 46 and 30 tuyères 1.25 in. in diameter; the blast-pressure is 14 lb., the matte used assays Cu 34.7,  $\text{SiO}_2$  0.3, Fe 32.2,  $\text{Al}_2\text{O}_3$  0.7, S 26 per cent.; the siliceous ore analyzes Cu 4.32,  $\text{SiO}_2$  66.0, Fe 4.82, CaO 0.69,  $\text{Al}_2\text{O}_3$  9.95, S 3.83 per cent.; 0.53 ton is used per ton of Cu. The life of a lining is good for 2000 tons of Cu. There are produced 34 tons of Cu per charge, 1.145 tons of slag (analysis given in Table 81) per ton Cu. The recovery of Cu in form of blister is 80 per cent.

(3) COPPER CLIFF, ONT.<sup>1</sup>—The Canadian Copper Co. converts its furnace matte with 23–29 per cent. Ni-Cu into refined matte with 80 per cent. Ni-Cu which is poured into cast-iron beds, 30 ft. long by 6 ft. wide made up of sections, when it is broken and shipped to be treated further. The works had ten acid barrel converters with shells 126 by 84 in., which were replaced in 1911 by five Peirce-Smith basic converters. A shell is 37 ft. 2 in. long and 10 ft. in diameter outside dimensions, has one central throat, and two lateral pouring openings. The vessel is manipulated by an oil- instead of a water-cylinder. There are 44 tuyères, 1.25 in. in diameter and 7 in. apart; beneath the throat there are no tuyères. The bottom lining is 15 in. thick, the roof 12 in., the tuyère-belt 24 in.; the inside length is 33 ft. 3 in.

In starting, a charge of 60 tons of furnace matte is given and followed by 10 tons of quartzite, the blast is turned on for  $1\frac{1}{2}$ – $3\frac{1}{4}$  hr., the slag poured, and at the same time 5–6 tons of furnace matte introduced to be followed by 3 tons of quartzite, when the slag has been removed; the vessel is blown for 40 min. The cycle of operations is repeated until 300–400 tons of furnace matte have been introduced, and 70–80 tons of converter matte produced, which takes 30–50 hr. blowing-time.

A comparison of acid and basic work is given in Tables 83 and 84.

TABLE 83.—WORK OF ACID BARREL CONVERTERS WITH CANADIAN COPPER CO., 1911

Month	Furnace matte, Ni-Cu, per cent.	One ton converter matte requires			Furnace-matte, tons
		Quartzite, tons	Clay, tons	Hour.-min. blowing on one shell	
July.....	29.00	1.10	0.52	2-01	4.45
Aug.....	28.65	1.40	0.47	1-56	4.66
Sept.....	25.75	1.46	0.52	1-46	4.90
Oct.....	24.35	1.67	0.77	2-04	6.10

<sup>1</sup> Browne, *Tr. Canad. Min. Inst.*, 1912, xv, 115 and Private Notes, 1912.

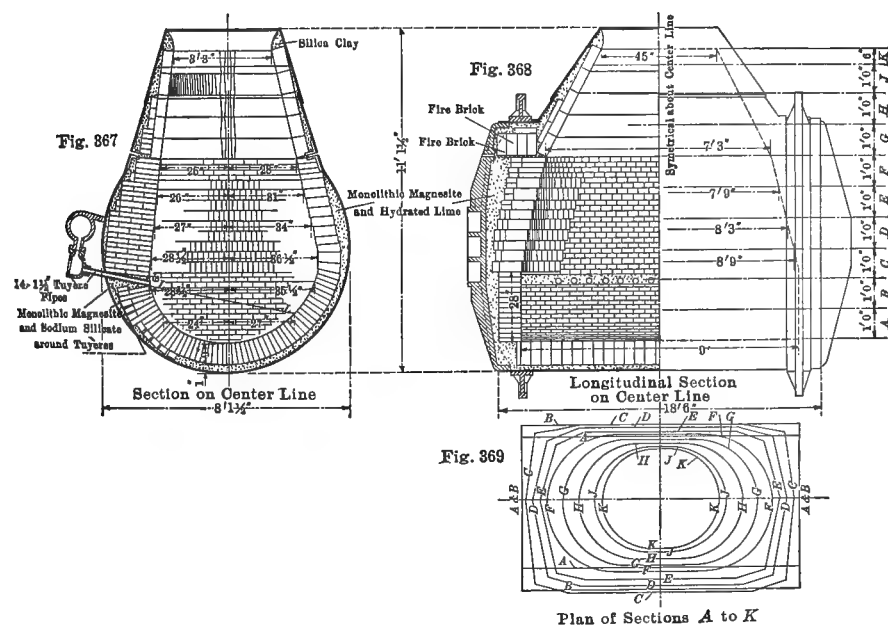


TABLE 84.—WORK OF PEIRCE-SMITH BASIC CONVERTER WITH CANADIAN COPPER Co., 1911

Month	Furnace matte, Ni-Cu, per cent.	One ton converter matte requires			
		Quartzite, tons	Rock, tons	Hour.-min. blowing on one shell	Furnace-matte, tons
July.....	29.00	0.77	0.57	0-23	3.16
Aug.....	28.65	0.71	0.50	0-26	2.85
Sept.....	25.75	0.86	0.43	0-17	3.35
Oct.....	24.35	0.97	0.85	0-24	3.95
Nov.....	23.70	0.86	0.77	0-25	3.72

A striking feature is the larger amount of furnace-matte the acid converter requires than the basic, the difference being due to the excessive slopping and spilling with the acid vessel.

**175. The Anaconda Basic Converter.**—Since 1910 the Washoe works at Anaconda have had in operation as basic converters their former acid vessels (§ 160) lined with magnesite brick. In Figs. 367-369 are given the form and lining of the vessels in use.



FIGS. 367-369.—Anaconda basic converter.

The leading change in form is that the tuyère-pipes are placed tangentially with the lower circle, and that the diameter has been increased from  $\frac{3}{4}$  in. to  $1\frac{1}{4}$  in. The shell and tuyère-belt are lined with magnesite mixtures which carry the magnesite brick. The shell-mixture consists of crushed magnesite brick,  $\frac{1}{4}$ - $\frac{1}{2}$  in., slaked lime, and enough water to make a plastic mass. This is

rammed to furnish a firm but elastic support for the brick. The brick used are the standard 9-in. arch, side- and end-wedge forms; the mortar is the undersize ( $< \frac{1}{4}$  in.) of the crushed bats, used in preparing the shell-mixture, ground fine and mixed with milk of lime to form a thin gruel. The tuyère-belt is packed with a mixture of finely ground magnesite, furnished by the manufacturer, and 20 per cent. of a 40-per cent. solution of sodium silicate. This packing insures a tight joint around the tuyère pipes, which wears as well as magnesite and does not spall as much in punching the tuyères as does magnesite brick.

A newly lined converter is dried and warmed with a wood fire in about 8 hr., when the ashes have been removed. A small charge of white metal is poured in, blown to copper, and the copper poured. The matte and metal fill any crevices and cement together the brick. The converter is now ready for regular work. In this there are first poured in 8 tons of matte, followed by 3500 lb. of dry siliceous ore;<sup>1</sup> the converter is turned over and blown 40 min.; without moving any slag, the second charge of 8 tons of matte and 3500 lb. ore is introduced, the amount of ore being varied to furnish a slag with  $\text{SiO}_2$  25-30 per cent.; the two charges together are then blown to white metal, the slag is poured and skimmed, and the white metal blown to copper in the usual way. Allowing the slag to accumulate retards oxidation and thus prevents overheating; a charge temperature exceeding  $1150^\circ \text{C}$ . quickly eats out the lining.

An average analysis of the matte blown in five months showed Cu 43.15,  $\text{SiO}_2$  0.3, Fe 25.55, S 24.82; one of the second-class ore used as flux:  $\text{SiO}_2$  61.45, FeO 12.48,  $\text{Al}_2\text{O}_3$  7.67, CaO 0.75, Cu (?), S 11.85; and of the slag produced:  $\text{SiO}_2$  26.5, FeO 55.4,  $\text{Al}_2\text{O}_3$  3.3, CaO 0.82.

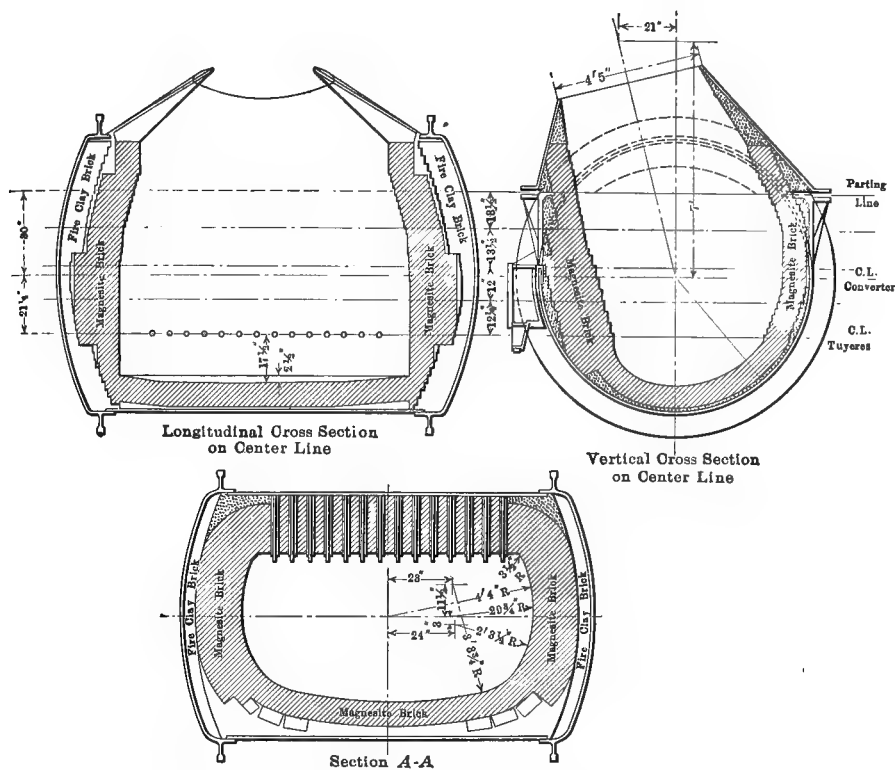
A  $\frac{3}{4}$ -in. bar is used for the regular punching of tuyères; at the end of a blow a  $1\frac{1}{4}$ -in. bar replaces the  $\frac{3}{4}$ -in. in order to remove all adhering matte so that the converter starts on the next blow with a clear  $1\frac{1}{4}$ -in. tuyère opening.

In the acid practice a lining stood 16 hr., having served to blow 50 tons of 43-per cent. matte; the life of a basic lining is good for 20,000 tons of matte. During this period the lining is patched when necessary, by removing the vessel from the stand, placing with a long-handle spoon stiff tuyère-belt mixture in front of the defective part and patting it down until it becomes quiet, *i.e.*, until the water has been driven off by the heat of the lining, which also hardens the mixture so that it stands as well as a new brick.

THE STEPTOE VALLEY SMELTING AND REFINING CO., McGill, Nev., has in addition to the two Peirce-Smith converters (page 344) three acid shells which have been lined with magnesite brick in a manner somewhat different from those at Anaconda; they are represented in Figs. 370-372. The shell, 96 by 150 in., with mouth about 42 in. in diameter, has fourteen tuyère-pipes 1 in. in diameter placed  $17\frac{1}{2}$  in. above the deepest point of the covered lining. The magnesite lining, thicker at the tuyère side than opposite and heavy at the ends, has an expansion space filled with clay; the cylindrical part of the lining is built on the clay except at the tuyère-belt where the tuyère-blocks are in contact with the shell; in the heads the clay is backed by fire-brick built against the plate-iron.

<sup>1</sup> Dope-Bucket of Anaconda, *Eng. Min. J.*, 1914, XCVII, 761.

The material charged and the manner of operating are similar to those in the Peirce-Smith converter. A stall works with a blast-pressure of 14 lb., produces from matte, with Cu 35 per cent., 20.5 tons of blister copper per day, uses 0.55 tons of ore ( $\text{SiO}_2$  66, Cu 4.32 per cent.) per ton of blister copper, makes 1.145 tons of slag ( $\text{SiO}_2$  23 per cent.) per ton of blister, and recovers 80 per cent. of the Cu.



FIGS. 370-372.—Steptoe barrel-converter lined with magnesite.

THE CANANEA CONSOLIDATED COPPER CO., Cananea, Sonora, Mexico, has a feature of special interest with its horizontal converters, 96 by 135 in., now lined with magnesite, in that it blows into them, by the Day system, high-grade fine concentrates. This method of treatment appears very advantageous if one calls to mind the clouds of dust arising when such material is poured into the converter from a boat or ladle, and when later the converter is turned over.

A screen analysis of Miami concentrate which is thus blown in shows that 50 per cent. is finer than 200-mesh; the chemical analysis gives  $\text{SiO}_2$  18.4,  $\text{Al}_2\text{O}_3$  4.5, Fe 12.0, CaO 1.0, Cu 38.0, S 21.6 per cent. The concentrate is dried in a three-hearth 16-ft. MacDougall furnace, with shaft making 3 r.p.m., at the rate of 150 tons in 24 hr., with a consumption of 8-10 bbl. oil, and an attendance of one feeder in 10 hr., and one furnace-man with two helpers in an 8-hr. shift.

The apparatus in connection with the converter consists of converter hood and balloon flue as shown in Fig. 373. The storage tank with a capacity of 35 tons of dry concentrate receives the material, and delivers some of it at intervals through valve into the pressure tank, which is connected top and bottom through a  $1\frac{1}{2}$ -in. pipe with air under a pressure of 60 lb. The lower pipe is joined by a rubber hose to the 1-in. inlet-pipe of the converter, provided with a Shelby valve.<sup>1</sup> It is through this single pipe that the concentrate is blown in short

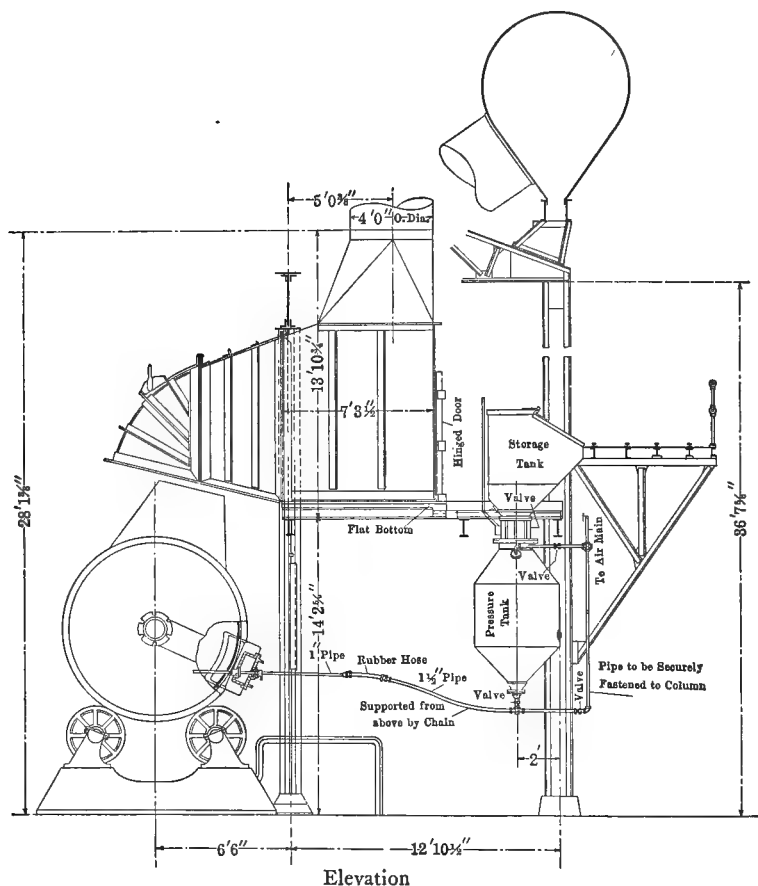


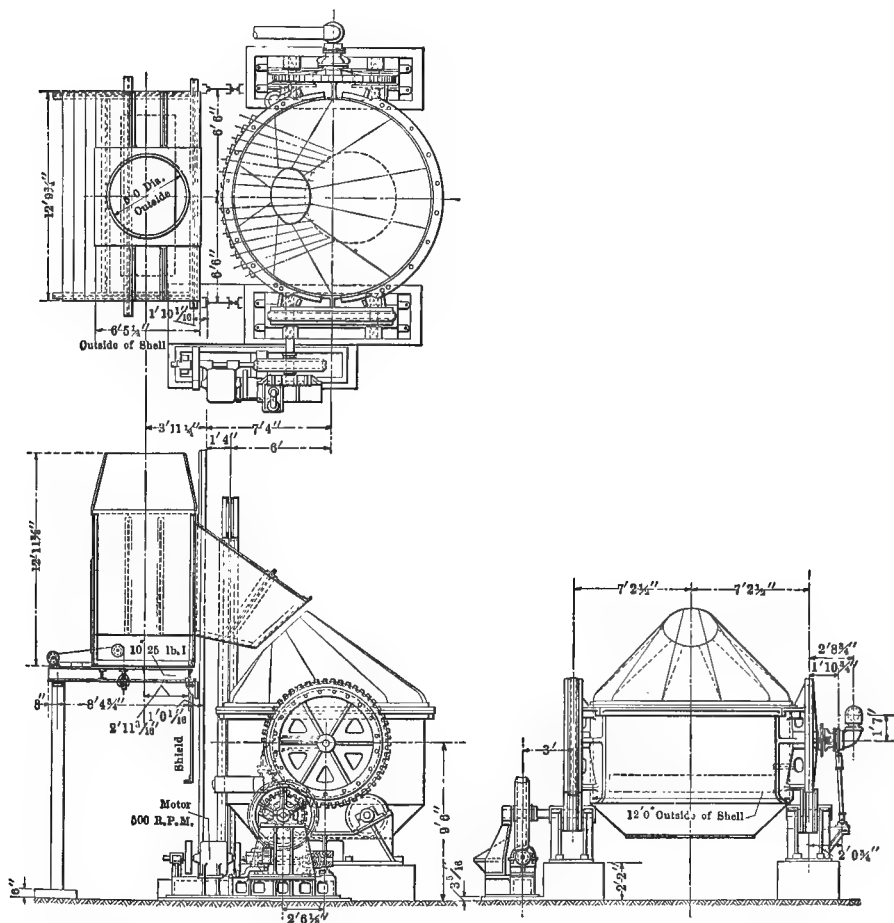
FIG. 373.—Day system of blowing concentrate into converter, Cananea.

periods at the rate of 100 lb. per minute, the man at the valve regulating the flow. If the periods last too long or follow one another at too short intervals, the slag in the converter becomes sticky, and in the end the converter too cool; the remedy lies in the feeding of the concentrate and in pouring in fresh hot matte.

At first, the use of this fine material increased the loss in metal by dusting,

<sup>1</sup> *Eng. Min. J.*, 1907, LXXXIII, 854.

but since the condensation plant has been enlarged, the dust-loss is not greater than when concentrate was not used. In the filtering experiments carried on to ascertain the loss, the dust was collected in settling boxes and in bays of the filter-bags. The dust collected in the boxes formed by weight 24.7 per cent. of the total; assayed Cu 22.87. Pb 8.66 per cent., Ag 18.92 oz.; and contained 86.5 per cent. of the Cu that entered the experimental plant. The part



FIGS. 374-376.—General arrangement of Gréat Falls basic converter.

collected in the bays from the bags formed 75.3 per cent. of the total; assayed Cu 1.17, Pb 15.00 per cent., Ag 14.26 oz.; and contained 13.5 per cent. of the entrained Cu.

**176. The Great Falls Basic Converter.**<sup>1</sup>—In 1897 a 7-ft. converter, similar to the one shown in Figs. 322-324, having eight  $\frac{3}{4}$ -in. tuyères was lined with magnesite, run for a short time with matte and siliceous ore, and some metallic

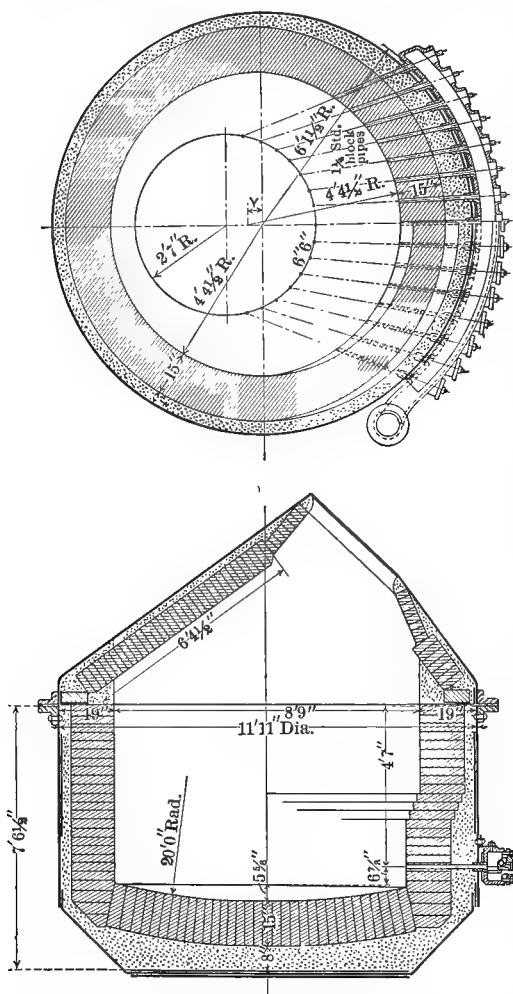
<sup>1</sup> Wheeler-Krejci, *Tr. A. I. M. E.*, 1913, XLVI.

copper produced; in 1906 chrome brick was tried at the tuyère-belt of the acid vessel; the start with the present regular basic practice was made in 1911 with a 12-ft. vessel; in 1912 the 20-ft. converter was put in blast; in 1913 it took the place of the preceding vessels. The improvements made here in converting are characterized by an increase in diameter and a shortening of the height of

the vessel, and by an increase in the diameter of tuyères.<sup>1</sup> A larger capacity of vessel and a larger volume of air blown into it, have resulted in reducing the number of vessels and the time required for blowing charge; combined they have diminished the cost of plant and of operation.<sup>2</sup>

The general arrangement of the converter with hood and gas-delivery pipe is given in Figs. 374-376. The vessel has at either end a short trunnion shaft attached to a friction-wheel running on a pair of friction-rollers carried by a roller-stand. One of the friction-wheels has a spur-wheel driven by a pinion, the shaft of which carries at the opposite end a worm-wheel engaging with a double-thread worm attached to the shaft of the electric motor; the break-band is not shown. On the opposite side is the wind-pipe connection delivering the air from the blowing engine to the wind-box and tuyères.

The 12-ft. basic vessel, 13 ft. 8.5 in. high, shown in horizontal and vertical sections in Figs. 377-378<sup>3</sup> (the number of tuyères has become the model for most of the new installations and the replacements in established plants. The 20-ft. basic vessel, 17 ft. 7.75 in. high, shown



FIGS. 377-378.—Great Falls 12-foot basic converter.

<sup>1</sup> Moore, *Bull.* 83, *A. I. M. E.*, Nov., 1913, p. 2666.

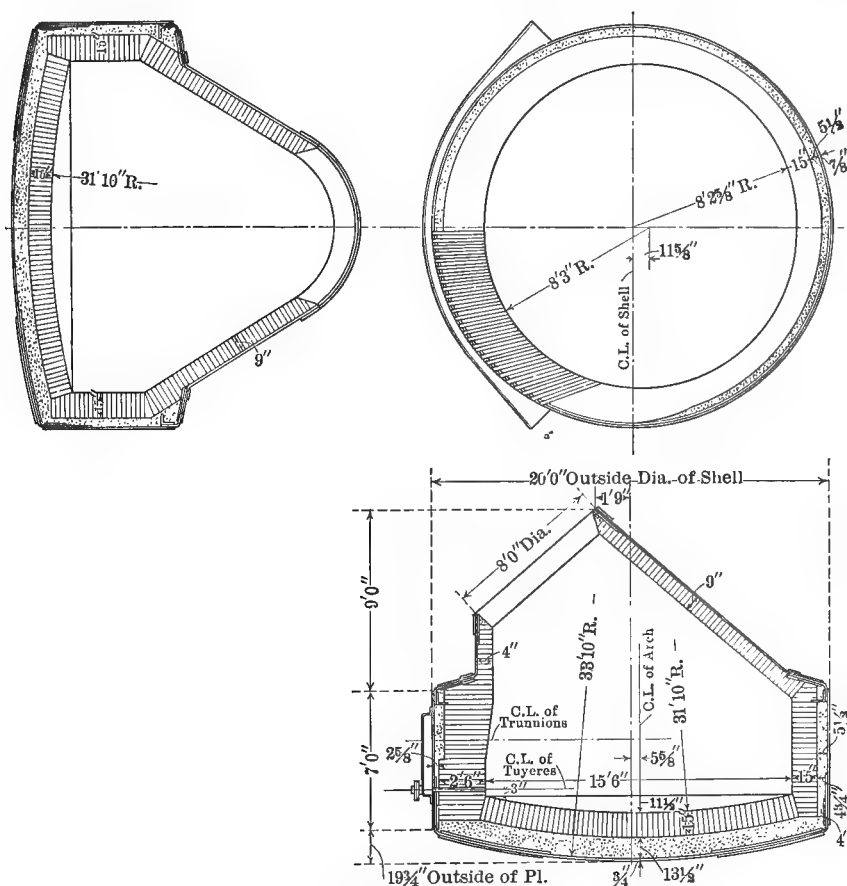
<sup>2</sup> Haas, *op. cit.*, p. 2656.

<sup>3</sup> Canaea, 12-ft. Converter, *Eng. Min. J.*, 1914, xcvi, 809.

in one vertical and two horizontal sections in Figs. 379–381 is so far confined to Great Falls.

It may be noted that the heights of these basic vessels are small as compared with the earlier acid; experiments had shown that taller vessels were not as satisfactory.

It is important that the mouth be of ample size; 6 ft. 6 in. in diameter for 12-ft. and 8 ft. for the 20-ft. have proved to be good figures. The advantages



FIGS. 379–381.—Great Falls 20-foot basic converter.

of a large mouth are, that the gases escape freely, that it is easy to charge liquid matte and solid ore, that there is less tendency to form crusts than with a small one, and that the crusts when formed are easily removed. If the diameter of the mouth exceeds the dimension advocated, there is an excessive loss of heat, which reduces the amount of material that can be melted by the heat of the charge.

The linings and cavities of the two converters are shown clearly in the figures; the lining is backed by a mixture of ground magnesite and sodium silicate;

the tuyère-belt is packed with a grout of a similar composition. The position, number and size of tuyères and their material have been the subject of many experiments. The conclusions reached are, that there should be at least 5 in. from the lowest point of tuyères to that of the bottom and that there should be enough copper at the finish of a blow to cover the tuyères; the 12-ft. vessel has 12.5 in., the 20-ft. 11.5 in. The results obtained with a greater and smaller number of tuyères of different sizes have shown that 12- and 20-ft. converters should have tuyères 2.25 in. inner diameter, and that the former does its best work with 26 and the latter with 62 pipes. As to the material, tuyère-pipes in the shape of cast blocks of copper worked well while blowing for white metal; they melted while blowing for blister copper. Heavy copper tubes are used at present. They fit into cast-steel blocks attached on the outside of the converter sheet; the space between the pipes is packed with a mixture of calcined magnesite and sodium silicate.

The amount of air blown into a 12-ft. vessel is about 11,000 cu. ft. per minute.; the 20-ft. vessel takes as much as 22,000 cu. ft. while blowing for blister, and about 18,000 while blowing for white metal. With these amounts the air efficiency, determined by analysis of gases taken from converter, ranges from 83.3 to 100 per cent., the lower figure coming from the end of the blister-stage, the higher from the slag-forming stage.

A study of the mechanical effects of the blast upon the molten matte has shown: (1) that the air penetrates the charge only for a short distance and then rises to the surface in larger or smaller bubbles depending upon the sizes of the tuyère-pipes, and (2) that the surface of the charge travels upward away from the tuyères toward the front, descends there toward the bottom, and returns across the bottom toward the tuyères.<sup>1</sup>

In starting a newly lined converter, *e.g.*, the 12-ft., the lining is dried and warmed with a wood fire for 36–48 hr.; the ashes are removed, and two ladles or 16 tons of matte (Cu 35 per cent.) poured in; the vessel is turned over, blown 2–3 min., and turned down to see the effect the blow has had on the brick lining. This operation is continued with additions of fresh liquid matte and with extensions of the duration of the blows until the cracks between the bricks have been filled and the surfaces so coated that the individual bricks cannot be recognized; the remaining matte is poured off, and the converter left undisturbed for a few hours to harden the matte in the crevices and the coating on the outside of the brick.

The vessel is now ready for normal work. In this there are charged two ladles or 16 tons of liquid matte, then 3700 lb. siliceous ore (Cu 3.5, SiO<sub>2</sub> 57.8, FeO 13.0, Al<sub>2</sub>O<sub>3</sub> 11.0 CaO 0.1, S 12.1 per cent.); the blast is started, the vessel turned over and blown for 30 to 40 min. with a pressure of 14 lb.; the slag formed is poured off. There is now poured in one ladle or 8 tons of matte and shot in 1800 to 3700 lb. of ore depending upon the grade of the matte, followed by 1.0–2.5 tons of converter cleanings and cold matte, all of which reduce the temperature of the bath; the vessel is again blown and skimmed. The opera-

<sup>1</sup> See also Haas, Nov., 1913, *Bull. A. I. M. E.*



tions are repeated until five or six ladles of liquid furnace matte have been introduced, and the converter matte has been brought forward to near the white-metal stage (Cu 70-75 per cent., recognized by its behavior on the rabble); the slag formed is poured off as much as possible and the rest skimmed; "dope" are fed in the form of scrap copper, white metal, and cleanings which reduce the temperature of the bath, which is now blown to a finish in 5-6 min. for every ton of copper in the vessel (12-14 tons of Cu or 18 tons of white metal).

The tuyères are punched more or less continually, less so during the slagging, than the blister-stage.

The progress in the process is usually judged by the flame; when in doubt, the vessel is turned down and the matte examined, or the copper is tested on the rod.

The actual blowing-time is 20 min. per ton of copper produced; a charge with matte of 38.9 per cent. Cu takes 8.5 tons of ore (Fe 10, Cu 3.5 per cent.), or 0.7 tons of ore per ton of Cu; the charge produces 12-14 tons of Cu.

The converter copper is poured into ladles and transferred to the copper-casting machine (Figs. 353-354); the converter-slag ( $\text{SiO}_2$  19.7, FeO 60.7,  $\text{Al}_2\text{O}_3$  6.3, CaO 1.3, MgO 0.25, Cu 1.6-2.0, S 2.0 per cent) is also poured into a ladle and handled in the slag-casting machine (Figs. 350-351).

A new departure has been made by Wheeler and Krejci<sup>1</sup> with the 20-ft. basic converter at Great Falls, Mont., in that they coat the magnesite lining with a mixture of fused oxidized iron (magnetite ?) and slag which is formed by blowing matte at a low temperature either alone or in the presence of a small amount of  $\text{SiO}_2$ . A newly-lined converter is brought slowly to a bright red, charged with liquid matte of a low grade, say 35 per cent. Cu, blown for 10-15 min., whereupon cold matte is added to reduce the temperature. These operations are repeated until the matte in the vessel has been brought forward to white metal, which is then poured. The brick of the empty vessel will be found to have been coated with what may be briefly called magnetite. A fresh charge of liquid matte is given and a little less siliceous ore added than in regular work; the charge is blown in the usual way, and is followed by other similar charges until the coating has become so thick that all joints of the brickwork have disappeared. The thickness is regulated by the temperature of the converter and the percentage of  $\text{SiO}_2$  of the slag.

## V. THE SULPHIDE COPPER SMELTING PLANT

**177. General Arrangement of Plant.**—The general characteristics of modern smelteries treating sulphide copper ores are: the large scale of operations demanding mechanical handling of materials in the different departments, and the combination, wherever feasible, of blast- and reverberatory furnace smelting of ore followed by converting of matte into blister copper. With most blast-furnaces the coarse raw ore is smelted by the partial pyritic process;

<sup>1</sup> *Bull. A. I. M. E.*, Feb., 1914.

Discussion, *Eng. Min. J.*, 1914, xcvii, 431 (James), 530 (Krejci), 628 (Howard), 724 (Williams), 821 (Merton, Krejci).

it is the exception that coarse ore undergoes a preliminary oxidizing roast. The fine ore or concentrate to be smelted in the reverberatory furnace is usually first rough-roasted in a mechanical furnace.

The flow of materials, Fig. 382, and the plan, Fig. 383, of the Washoe smelting at Anaconda show in general the sequence of operations and the locations of the several divisions.

At this plant<sup>1</sup> first-class ore, which is coarse and contains 10 per cent. Cu and over, goes direct to the blast-furnaces (§ 90); second-class ore, with perhaps 3 per cent. Cu, passes through the concentrating plant and goes in the form of concentrate, with about the same tenor in Cu as first-class ore, to the MacDougall-roasting furnaces (§ 64). The roasted concentrate ("calcine") is smelted in

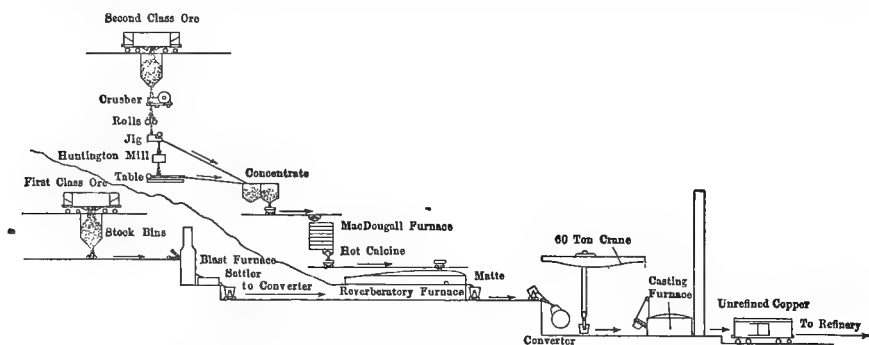


FIG. 382.—Flow of materials through the Anaconda smelter.

reverberatory furnaces (§ 131). The matte from the blast- and reverberatory furnaces is hauled by compressed-air locomotion on the same level in ladles to the converters (§ 175), whence the blister copper is poured into ladles and transferred by means of traveling electric cranes to reverberatory casting furnaces, where it is fire-refined, and shipped in the form of anode-copper to be refined electrolytically.

The plan, Fig. 383, of the works shows the location of the different departments. The sampler, the concentrator, the roaster, the blast-furnace, the reverberatory furnace, and the converter-divisions, are in separate buildings. Communication between them is effected by thirteen compressed-air locomotives working under a pressure of from 800 to 900 lb. They handle daily about 13,000 tons of materials, which represents a daily capacity of 7000 tons of ore and a production of 500,000 lb. blister copper.

The new works of the International Smelting and Refining Co. at Tooele<sup>2</sup>

<sup>1</sup> Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 251.

Austin, *op. cit.*, 1906, XXXVII, 431.

Correspondent, *Mines and Minerals*, 1907, XXVIII 131, 248.

"A Brief Description of the Washoe Smelter" by members of the Anaconda Copper Mining Co.'s Staff, Anaconda, Mont., 1907.

<sup>2</sup> Palmer, *Min. World*, 1910, XXXII, 419.

Repath and McGregor, *Met. Chem. Eng.*, 1911, IX, 15.

Thomson-Sicka, *Tr. A. I. M. E.*, 1913, XLVI.

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are built on the same general plan as the Washoe plant excepting that they smelt exclusively concentrates in reverberatory furnaces, and that the matte is tapped direct into the converters. This last feature has been changed, as it was found impossible to judge of the amount of matte a converter received. The matte is therefore weighed as is the case in other works.

The smeltery of the British Columbia Copper Co. at Greenwood, B. C. which smelts in the blast-furnace only and converts the resulting matte, has

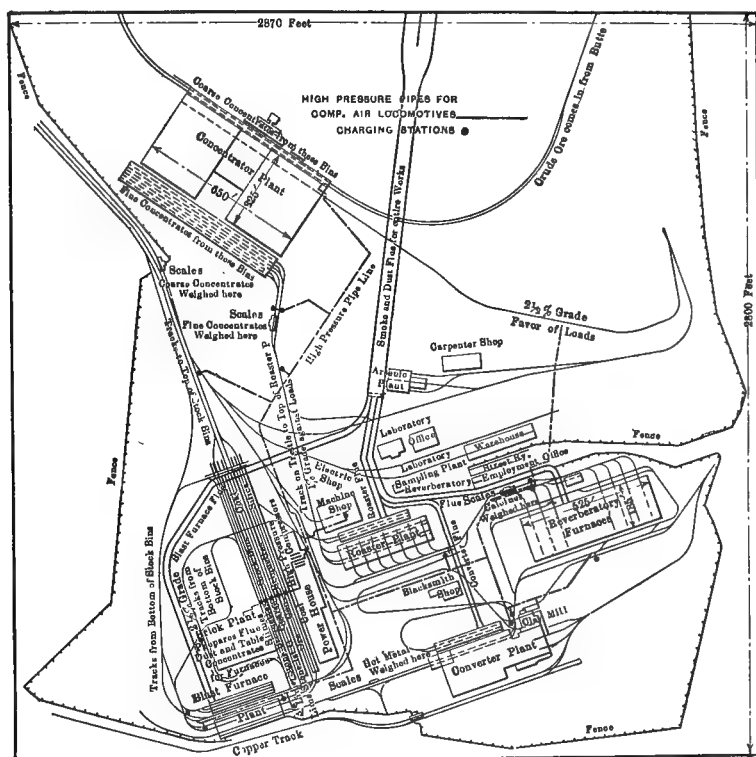


FIG. 383.—General plan of Anaconda smeltery.

been described with drawings by McAllister.<sup>1</sup> It resembles in general arrangement the plant of the Canadian Copper Co.<sup>2</sup>

An early plan of the smeltery at Great Falls, Mont., is given by Higgens<sup>3</sup> and a later illustration is that of Fig. 238. The ore-treatment is similar to that of the Anaconda works.

The Flow-sheet (1912) of the Cananea Consolidated Copper Co.'s smelting, shown in Fig. 384, gives in detail, with diagrammatic sketches of apparatus, the complications of the work in a modern plant treating sulphide ore by blast- and reverberatory-furnace smelting followed by converting. It shows

<sup>1</sup> *Eng. Min. J.*, 1911, XCI, 1011.

<sup>2</sup> *Eng. Min. J.*, 1903, LXXVI, 1008; Browne, *Canad. Min. J.*, 1907, XXVIII, 305.

<sup>3</sup> *Eng. Min. J.*, 1909, LXXXVII, 156.

how the raw materials enter each division and gives the paths of the intermediary and finished products. The operations of the several divisions have been discussed in the preceding pages. The large number of roads indicated in the figure, at first bewildering, becomes simple and clear when followed step by step. A general review is therefore unnecessary.

The feature that is unique is the Dwight-Messiter Ore-bedding System<sup>1</sup> recently introduced also at the smelter of the Calumet & Arizona Mg. Co.<sup>2</sup> and the Tennessee Copper Co.<sup>3</sup> by means of which ores for the blast-furnaces are sampled, bedded, reclaimed, and delivered mechanically to the blast-furnace storage bins.



Fig. 385.—Overhead skeleton structure of Dwight Messiter Ore-bedding System, Cananea.

In the flow-sheet of Cananea, the narrow-and standard-gauge railroad brings all blast-furnace materials, such as coarse ore, coarse concentrates, fluxes, and secondaries (intermediary products) and delivers them over scales to nineteen bins. From the hoppers of these the materials are supplied by traveling shaker-feeds to the conveyor belt, No 1, which discharges onto a grizzlie whence the oversize goes to Farrel crushers, and the undersize as well as the discharge of the crushers to conveyor belt, No. 2, and the Bishop-Vezin sampler. The sample goes by the 20-in. sample conveyor to the sampling mill, while the rejects return to the main stream by bucket elevator and conveyor No. 3. Trippers at the junctions of conveyor, No. 3, and belts 4<sup>A</sup>, 4<sup>B</sup>, 4<sup>C</sup>, deliver the materials to these belts, which pass over the center lines of the three storage beds and deposit the material in

<sup>1</sup> Woodbridge, *Eng. Min. J.*, 1906, LXXXII, 624.

Messiter, *Min. Sc. Press*, 1907, XCV, 528; 1909, XCVIII, 361.

Herrick, *Mines and Minerals*, 1909-10, XXX, 65; Pamphlet, Robins Conveying Belt Co., New York.

<sup>2</sup> Editor, *Eng. Min. J.*, 1912, XCIII, 682.

<sup>3</sup> Wierum, *Eng. Min. J.*, 1913, XCVI, 435.

long narrow strips. A bed holds 8500 tons of ore. A high-speed traveling tripper moves constantly to and fro over a bed upon an overhead skeleton structure, Fig. 385, and deposits the materials uniformly so that all portions of any cross-section of the bed will have the same composition. On the floor and along the sides of each bed are rails upon which travels the reclaiming machine, Fig. 385, at a speed of  $\frac{5}{8}$  in. per minute. The machine is a bridge-shaped structure spanning the width of the bed and reaching beyond it on one side to cover the conveyor belt placed there in a trench, Fig. 385, and Fig. 384 belts  $5^A$ ,  $5^B$ ,  $5^C$ . In the front of the bridge is suspended a scraper conveyor which operates in a trough consisting of a bottom and a back plate. The trough is placed at an angle to the axis of the conveyor and carries at the front plow-shaped extensions. In front of the machine is mounted an adjustable triangular harrow having a reciprocal motion to dislodge the ore, that it may run down the face of the bed, fall on the bottom plate of the conveyor, be carried along to the discharge end, and fall through a short chute onto the belt conveyor in the trench. The belts  $5^A$ ,  $5^B$ ,  $5^C$ , in the trenches deliver the ore-mixture to conveyor No. 6, whence the material travels over belts No. 7 and No. 8 to be delivered by movable trippers into the eight 80-ton steel storage bins of the blast-furnaces, Figs. 171-174.

It takes 4 days of 10 hr. each to deliver the 8500 tons of ore forming a bed; the labor required is 1 ore-bin man, 2 helpers, 4 men on belts, 1 crusher-man, and 5 to 6 laborers. A bed is reclaimed at the rate of 150 tons per hour by 1 man on machine, 1 helper,  $\frac{1}{3}$  oiler and 1 tripper. The cost of handling from unloading to delivery into the blast-furnace bins, including labor, power, repair, and belt removal, is 9 cents per hour.

The handling of ores at the Copper Queen Smelter, Douglas, Ariz.,<sup>1</sup> form another instance of the application of machinery to bedding and reclaiming. In the yard there are five ore pits, 40 ft. wide and 11 ft. deep; four are 825 ft. long, the fifth 1000 ft. Ore from the Copper Queen mine is received in 14-car trainloads. The cars are loaded at the mine by means of belts and trippers;<sup>2</sup> the contents are therefore of uniform composition and can be placed in the pits one lot above the other in layers and form a uniform mixture. Other ores are spread over the mixture in order to obtain a self-fluxing charge. The bed in a pit is reclaimed by means of a No. 4 Thew steam-shovel (Lorain, O.) which has a capacity of 100 tons per hour. The shovel is set to dig to the level of the track, it loads a train of 20 blast-furnace charging cars, each with a measured amount of about 2700 lb. mixture. The train is hauled under 20 coke-hoppers, where each car receives a weighed amount of fuel, and then to the feed-floor on either side of a row of 10 blast-furnaces (Table 82) where there are two tracks, one for full, the other for empty cars.

**178. Cost of Plant.**—Most of the earlier copper smelteries were connected with little mines and had small capacities. The ores treated were comparatively

<sup>1</sup> Woodbridge, *Eng. Min. J.*, 1906, LXXXII, 242.

Douglas, *Tr. Inst. Min. Met.*, 1912-13, XXII, 532.

<sup>2</sup> Milton, *Mines and Minerals*, 1909, XXX, 148.

rich in Cu, so that the cost of treatment could be high and still leave a satisfactory profit. The Cu-content of the ores mined has grown smaller, the mines have had to be worked on a larger scale, the smelteries have had to work larger quantities of ore with a diminishing copper-content. In other words, the capacities of modern smelteries have become very large. This calls for large expenditures of capital for building a plant and an equally large capital for operating. The figures given in Table 85 are reliable estimates furnished by the best of authority.

TABLE 85.—CAPITAL OF ESTABLISHMENT AND OF WORKING FOR SULPHIDE COPPER SMELTERIES

Character of plant	Product in 24 hr.	Necessary capital:		Annual product:	
		Of establishment <sup>1</sup>	Of working (additional) <sup>2</sup>	Amount and kind	Value
A. Copper blast-furnaces, partial-pyritic smelting, 1000 tons of ore per 24 hr.	100 tons, 45-per cent. copper matte.	\$1,250,000	\$1,000,000	36,500 tons matte	\$3,285,000
B. MacDougall roasting and reverberatory smelting, 1000 tons ore in 24 hr.	100 tons, 45-per cent. copper matte.	\$1,250,000	\$1,000,000	36,500 tons matte	\$3,285,000
C. Converting 45-per cent. copper matte, 200 tons per 24 hr.	90 tons blister copper.	\$250,000	\$2,000,000	32,850 blister Cu tons,	\$7,570,000

As regards the depreciation of a copper smeltery, Mathewson<sup>3</sup> estimates that, providing repairs are well kept up, the life of a plant is 20 years, *i.e.*, that 5 per cent. of the original cost of plant should be written off for depreciation. He also states that if a plant is dismantled, only 5.49 per cent. of the original cost will be recovered as salvage.

## B. SMELTING OXIDE COPPER ORES

**179. Smelting Oxide Copper Ore in General.**<sup>4</sup>—Oxide copper ores rich in copper used to be smelted in Arizona and New Mexico in water-jacket blast-furnaces, having internal crucibles, for black copper (96 per cent. Cu), and waste slag, with from 1.5 to 2.5 per cent. Cu.<sup>5</sup> The industry started about 1881,

<sup>1</sup> Capital of establishment: If the three operations A, B, C are combined in one plant a reduction of \$250,000 can be made from the above totals. All buildings are supposed to be fire-proof throughout and of best modern construction. The prices include all accessories necessary for the operation of such plants as A and B; plant C would be merely an addition to A and B, or A+B.

<sup>2</sup> Capital of working: If all three operations are combined in one plant, \$2,000,000 is sufficient for all working capital. The value of copper in form of blister is figured at 10 cents a pound. No values of silver or gold are included in the above estimates.

<sup>3</sup> *Eng. Min. J.*, 1906, LXXXII, 888.

<sup>4</sup> Douglas, *Min. Res.*, U. S. Geol. Surv., 1882, p. 261; 1883-84, p. 397; *Tr. A. I. M. E.*, 1909, XL, 422.

Wendt, *op. cit.*, 1886-87, xv, 25.

Austin, *Min. Sc. Press*, 1908, xcvi, 196.

<sup>5</sup> Channing, *Tr. A. I. M. E.*, 1910, xli, 885.



when the cost of coke was too high to permit charging enough fuel to make clean slags. Smelting the old slag dumps later on with sulphide ore showed<sup>1</sup> that in some instances the copper-content exceeded 2.5 per cent. viz., Globe 3.5, Morenci 4.5 per cent. At present rich oxide ore is mixed with sulphide material and smelted for matte, which is converted; poor oxide ore has been leached (§ 204).

Attempts have been made<sup>2</sup> to reduce to the metallic state the copper from a mixture of rich oxide ore and fuel by passing it through an inclined revolving cylinder heated internally from a fire-place at the lower end, and then separating the globules of copper by mechanical concentration. Such work can give only a small yield, and may be justified in regions where other processes are not feasible.

**180. Early Work in Arizona.**—Some of the leading facts of the former Arizona practice are given in Tables 86–89. The blast-furnaces were water-

jacketed throughout; most of them were circular in cross-section, only a few rectangular. In order to prevent the black copper from chilling, all furnaces had internal crucibles from which slag was tapped at intervals into slag-pots and black copper into pig-molds holding about 250 lb.

The Arizona copper furnace is shown in Fig. 386 and a pig-mold in Fig. 387. The furnace, 36 in. in diameter at tuyères, 54 in. at throat and 6 ft. working height, has the form of an inverted cone resting on a cast-iron bed-plate supported by four hollow cast-

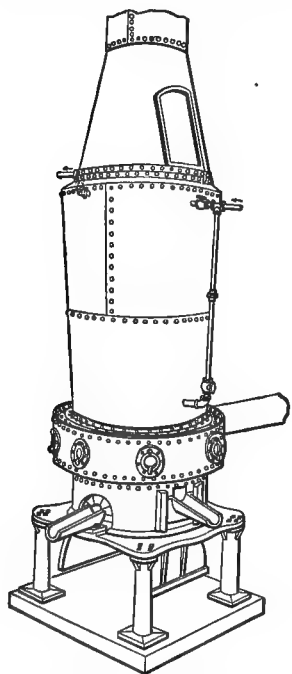


FIG. 386.—Arizona copper blast-furnace.

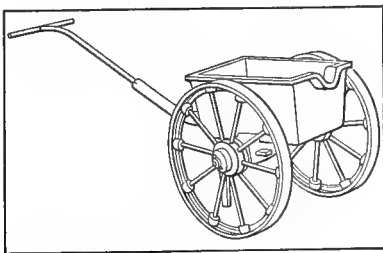


FIG. 387.—Copper mold.

iron columns. It is water-jacketed from the throat to below the wind-box; the water-space is 9 in. wide at the bottom and 4.5 in. at the top. The outer shell extends downward below the jacket and forms the side wall of the crucible. The water-inlet pipe, 2.5 in. in diameter, is usually at the center, and not both near bottom and top as seen in the figure. The feed-

<sup>1</sup> Douglas, *Tr. A. I. M. E.*, 1909, XL, 422.

<sup>2</sup> Experiments of Caspari-Flegel, *Metall-Erz*, 1913, X, 253.

water, under a pressure of 8 or 10 ft., strikes a deflecting plate so as not to impinge upon the inner shell; the overflow-pipe, 2.75 in. in diameter, is tapped into the top of the jacket; a 36-in. furnace takes 950 gal. water per hour, a 42-in. 1200 gal., a 48-in. 1500 gal. The crucible is 24 in. deep; its bottom is formed by two cast-iron plates hinged to the bed-plate; the lining reaching to the tuyères is brasque, or sand and burnt clay, or quartz and slag. The removable air-box, 10 in. above the slag-tap, has six bronze tuyère-openings; opposite each there is on the outer side a peep- and poking-hole closed by a cap provided with a mica shield. The feed-door is in the hood ending in the chimney, the blast-pipe ends at the wind-box, the metal-tap is 14 in. below the slag-tap.

Walker and Murphy<sup>1</sup> surrounded the crucible with an air-jacket to keep the walls cool and to warm the blast. This plan has not been adopted by others for obvious reasons.

The cost of smelting a ton of ore in 1892-94 at the works of the Old Dominion Copper Co. at Globe, Ariz., with two 36-in. blast-furnaces is given by Austin<sup>2</sup> as \$8.96 per ton yielding 260 lb. black copper

TABLE 86.—ANALYSES OF ARIZONA OXIDE COPPER ORE

Locality	Cu	SiO <sub>2</sub>	FeO	MnO	CaO	Reference
Longfellow.....	38.80	11.15	10.40	.....	.....	Wendt, <i>Tr. A. I. M. E.</i> , 1886-87, xv, 25
Longfellow.....	21.67	17.25	.....	7.43	.....	
Longfellow.....	17.17	26.80	13.76	7.49	.....	
Coronado.....	21.95	48.90	12.09	.....	.....	
Coronado.....	11.17	67.00	8.88	.....	.....	
Old Dominion.....	15.17	35.3	28.7	.....	22.2	Austin, <i>Min. Sc. Press</i> , 1908, xcvi, 196.

TABLE 87.—ARIZONA BLASTFURNACES FOR OXIDE COPPER ORE

Smeltery	Tuyère section, in.	Throat section, in.	Working height, ft.	Tuyères			Slag-tap above matte-tap, in.	Charge			Blast-pressure, oz.	Slag, Cu, per cent.	Reference
				No.	Diam, in.	Above slag-tap, in.		In 24 hr., tons	Cu per cent.	Fuel, per cent. of charge			
Copper Queen ..	36 diam.	54 diam.	6.0	6	3 and 5	10	14	47	12.9	17.0	10	1.27	Wendt
Old Dominion ..	36 diam.	.....	.....	6	3	.....	.....	56	17.3	13.2	10	.....	Douglas
Bisbee .....	42 diam.	54 diam.	6.5	6	4 and 5	8	12	50	.....	15.1	8	.....	Peters
Detroit .....	33×66	54×87	10.5	14	2.75	6	14	85	11.8	15.2	12	1.11	Howe
United Verde ..	36×90	48×90	9.0	10	3.50	11	24	.....	.....	.....	.....	.....	.....

<sup>1</sup> Walker, *Eng. Min. J.*, 1893, lvi, 619.

<sup>2</sup> *Min. Sc. Press*, 1908, xcvi, 196.

TABLE 88.—ANALYSES OF ARIZONA BLAST-FURNACE SLAGS

Smelter	SiO <sub>2</sub>	FeO	MnO	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Cu	CuO	S	Reference
Copper Queen.....	24.67	44.85	0.39	10.92	1.75	15.57	2.10	0.28		
Copper Queen.....	30.06	53.36	11.10	.....	.....	.....	0.15	1.02		
Detroit.....	34.34	32.27	8.05	10.13	2.30	11.64	.....	.....		Wendt, <i>Tr. A. I.</i>
Detroit.....	29.50	37.08	1.13	9.02	7.44	14.07	1.82	0.30		<i>M. E.</i> , 1886-87,
Prince.....	27.16	34.62	0.49	17.42	3.51	14.70	1.64	0.33		xv, 25.
Old Dominion.....	27.23	51.30	1.65	5.14	2.54	5.22	.....	3.76		
United Verde.....	35.79	37.89	.....	12.98	0.75	8.29	0.18	2.59		
Bisbee.....	28.0	29.0	.....	9.0	.....	27.0	1.32	.....		Howe, "Copper Smelting," p. 78

TABLE 89.—ANALYSES OF ARIZONA BLACK COPPER

Smelter	Cu	S	Fe	As	Sb	Bi	Ins.	Reference
Prince.....	95.00	0.44	4.23	.....	.....	.....	0.51	Wendt, <i>op. cit.</i>
Old Dominion.....	98.91	0.64	0.12	0.057	0.008	0.010	0.065	
Old Dominion.....	98.27	0.60	0.73	0.039	0.019	trace	0.060	Austin, <i>Min. Sc.</i>
Old Dominion.....	98.24	0.53	0.80	0.054	0.021	0.006	0.007	<i>Press</i> , 1908, xcvi, 196.
Old Dominion.....	97.52	0.69	0.97	0.052	0.014	trace	0.180	

C. SMELTING NATIVE COPPER ORE<sup>1</sup>

**181. The Ore.**—The discussion is confined to the smelting of Lake Superior ore (§ 45). This is passed through ore-dressing works, the products of which are treated, with some mass copper coming direct from the mines, in five smelting plants, viz., the Calumet & Hecla Mining Co., Hubbel, Mich., and Buffalo, N. Y.; the Quincy Mining Co., Ripley, Mich.; the Lake Superior Smelting Co., Dollar Bay, Mich.; and the Michigan Smelting Co., Houghton, Mich. The product of the ore-dressing works, called "mineral," contains three grades of material: barrel work, headings, and grades. The smelting works treat:

(1) **MASS.**—Pure copper with adhering rock, sorted at the mine, varying in weight from a few pounds to several tons; Cu 70± per cent.

(2) **BARREL WORK.**—Pure material, too large to go into mill, sorted at the mine and the mill (as the rock is fed to the stamps), consisting of pieces orange size and smaller; Cu 65-75 per cent.

(3) **HEADINGS.**—Pieces of clean copper, egg size, taken from the stamp-mortar; Cu 65-85 per cent.

(4) **GRADES.**—Concentrates varying from slime to walnut size; Cu. 20-70 per cent.

The average of the four classes of materials is about 70 per cent. Cu.

<sup>1</sup> Egleston, *Tr. A. I. M. E.*, 1880-81, ix, 678.

Douglas, *Min. Res.*, U. S. Geol. Surv., 1882, 259.

Cooper, *Proc. Lake Sup. Min. Inst.*, 1901, vii, 44.

Rickard, *Eng. Min. J.*, 1904, LXXVIII, 984 (also "The Copper Mines of Lake Superior,"

McGraw-Hill Book Co., New York, 1905, pp. 142-151).

White, *Eng. Min. J.*, 1905, LXXIX, 842.

Austin, *op. cit.*, 1906, LXXXI, 83.

Conant, *School Min. Quart.*, 1911, XXXII, 285.

The proportion which each of these four classes of materials forms, varies with the character of the deposit, whether conglomerate or amygdaloid, and with the practice of the concentration plant. In Table 90 are given two examples from the Michigan Smelting Co. for 1906 and 1911. Data from some of the other works, which are not for publication, are similar.<sup>1</sup>

TABLE 90.—PROPORTION AND COPPER-CONTENT OF SMELTING MATERIAL OF THE MICHIGAN SMELTING CO.

	1906		1911	
	Per cent., total	Per cent., Cu	Per cent., total	Per cent., Cu
Mass.....	11.5	68	5	70
Barrel work.....	6.2	68	5	65
Headings.....	15.1	90	30	85
Grades.....	67.2	68.72	60	50
Total and average....	100.0	71.82	100	62.25

**182. Process.**—The smelting process is essentially an oxidizing fusion in a reverberatory furnace, with or without the addition of some limestone as flux, in which the gangue is scorified and the slag skimmed as fast as it is formed. The oxidizing smelting is followed by a refining of the copper, either in the same or in another furnace into which the metal has been tapped. The refined copper is ladled or cast into commercial forms or into anodes. The reverberatory furnace ore-slag (Cu 12–15, SiO<sub>2</sub> 40, FeO 16, CaO 11, MgO 5, Al<sub>2</sub>O<sub>3</sub> 13 per cent.) is crushed and smelted with the necessary flux (limestone) in a blast-furnace in which the anthracite ( $\frac{1}{3}$  of the whole fuel) charged is intended to serve mainly as a reducing, and the coke ( $\frac{2}{3}$  of the whole) mainly as the heat-producing agent. The refining slags, Cu 30–35 per cent., sometimes are added to the ore-smelting charges. The “cupola copper” of the blast-furnace is tapped into molds to form blocks weighing 200–400 lb., and refined. The refining is usually carried on in a special furnace, as the cupola copper is impure (Cu 94± per cent.).

The waste-slag (Cu 0.75, SiO<sub>2</sub> 40, FeO 20, CaO 16, Al<sub>2</sub>O<sub>3</sub> 14 per cent.) is run through brick-lined forehearth into slag-pots, or is granulated, and goes to the dump. With the exception of slime concentrates, all the material received by a smelter goes straight into the reverberatory smelting furnace; the slimes are agglomerated for blast-furnace treatment, either by fusion in a reverberatory furnace, or by briquetting.

**183. The Reverberatory Furnace.**—The reverberatory smelting and refining furnaces have the general form of the English reverberatory smelting furnace; the main difference is that the hearth slopes from the fire-bridge to the flue, beneath which the refined copper is taken out either by ladling or by allowing it to run into a casting-ladle. In furnaces treating mass copper, part of the

<sup>1</sup> Parmelee, “Quincy Smeltery,” *Met. Chem. Eng.*, 1913, XI, 122.

roof can be, or formerly could be raised by a crane and swung to one side to permit charging of the mass. As this weakens the roof, and as there are now simple means of cutting up large pieces of copper, the hole in the roof has become the exception. Large pieces of mass copper, which are of less frequent occurrence than formerly, are often put aside until the roof of a furnace has to be renewed, when they are lowered onto the uncovered hearth.

The fire-bridge of a reverberatory furnace as well as the roof above it are provided with ports to admit the necessary air to the hearth.

The reverberatory furnace used thirty years ago had a capacity of from 7 to 9 tons of copper; the hearths were  $7 \times 12$  ft. and  $8 \times 14$  ft., and the respective fire-boxes  $36 \times 48$  in. and  $42 \times 42$  in. The capacities were later increased to 20 tons per day with a hearth  $11 \times 14$  ft. and a fire-box  $4 \times 4$  ft.; in recent years furnaces of larger capacities have been erected. A further improvement is the use of waste-heat boilers for utilizing the heat in the waste gases. Experiments with mechanical stokers have not given results which show clearly that they are more advantageous than hand-firing.

The dimensions of some reverberatory furnaces and the work done in them at Lake Superior are given in Table 91.

TABLE 91.—LAKE SUPERIOR REVERBERATORY FURNACES

	Michigan Smelting Co.	Calumet & Hecla Mining Co.		
		Hubbell, Mich.	Buffalo, N. Y.	Buffalo, N. Y.
			Melting	Melting and refining
Length of hearth, ft. in. ....	23' 3"	20' 6"	21' 0"	21' 2"
Width of hearth at bridge, ft. in. ....	7' 0"	6' 0"	8' 4"	8' 6"
Width of hearth at middle, ft. in. ....	14' 4"	13' 0"	13' 8"	15' 6"
Width of hearth at flue, ft. in. ....	0' 11"	3' 0"	4' 0"	5' 0"
Hearth area, sq. ft. ....	260	202	235	244
Hearth depth, in. ....	40"	9.5"	At side door	
			7"	18"
Hearth thickness, in. ....	27"	12"	14"	13"
Hearth material. ....	Brick and fused sand	Sand	Sand	Sand
Hearth support. ....	Concrete	Fire-brick arch	Iron plate and arch- brick	Brick
Grate, length, ft. in. ....	4' 3"	4' 0"	4' 10"	4' 6"
Grate, width, ft. in. ....	6' 2"	6' 0"	8' 0"	7' 6"
Grate, depth below top of bridge at bridge, ft. in. ....	3' 10"	2' 9"	3' 3"	4' 2"
Grate, depth below top of bridge at opposite end, ft. in. ....	3' 10"	2' 9"	3' 4"	4' 3"
Grate, area, sq. ft. ....	26	24	38.66	33.75
Ratio, hearth to grate area. ....	10:1	8.41:1	6.08:1	7.23:1
Roof, height above bridge, ft. in. ....	1' 8"	1' 7"	1' 10½"	1' 9"
Roof, height above hearth at bridge, ft. in. ....	5' 6"	2' 6"	3' 5"	3' 0"
Roof, height above hearth at flue, ft. in. ....	0' 6"	2' 0"	2' 1"	3' 3"
Bridge, width, ft. in. ....	4' 0"	3' 0"	3' 5"	3' 5"
Vulcuary (flue leading out of roof), ft. in. ....	2' 4" × 4'	4.5 sq. (feet)	3' 3" × 1' 6"	3' 3" × 1' 6"
Flue leading to chimney, ft. in. ....	2' 4" × 4'		1' 4" × 1' 6"	1' 4" × 1' 6"
Chimney, inside diameter, ft. in. ....	10' for all furnaces	3' × 3'	3'	3'
Chimney, height, ft. ....	250'	90'	83'	83'
Waste-heat boiler, number, kind, h.p. ....	One 250-h.p. Stirling	None	150-h.p. Cook	.....

TABLE 91.—LAKE SUPERIOR REVERBERATORY FURNACES.—*Continued*

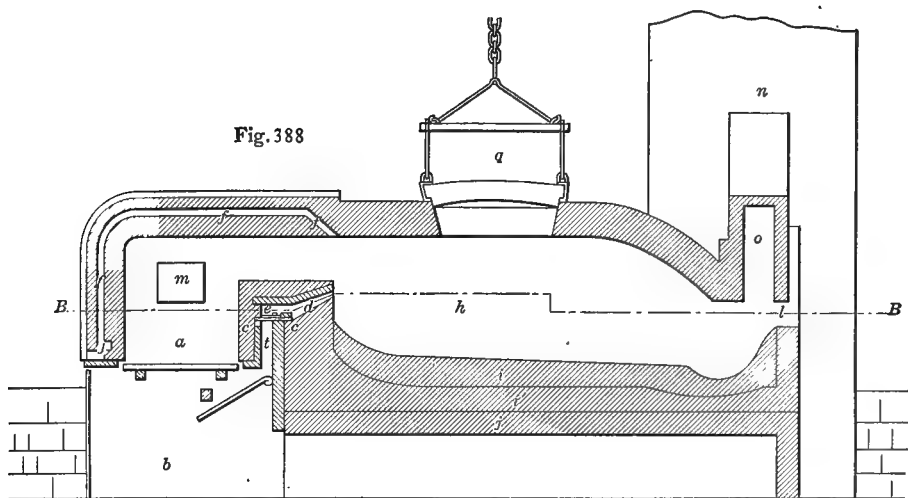
	Michigan Smelting Co.	Calumet & Hecla Mining Co.		
		Hubbell, Mich.	Buffalo, N. Y.	Buffalo, N. Y.
Charge, character, quantity.....	Molten cop- per, and cupola blocks	Mineral, mass barrel work	Mineral and	cathodes
Charge, time of working, total hr.....	22	.....	.....	24
Charge, time of charging, total hr.....	1	.....	.....	2
Charge, time of melting and raking, hr.....	8	.....	.....	16
Charge, time of fining, hr.....	6	.....	.....	1
Charge, time of poling, hr.....	■	.....	.....	2
Charge, time of ladling, hr.....	.....	.....	.....	2.5
Charge, time of casting, hr.....	4	.....	.....	.....
Charge, time of cleaning up and recharging, hr.....	1	.....	.....	2
Charge, tons in 24 hr.....	150	.....	.....	34
Charge, tons per sq. ft. of hearth in 24 hr.....	0.6	.....	.....	.....
Charge, tons per ton coal.....	15	.....	.....	4
Coal, ash, per cent.....	9	.....	.....	7.5
Coal, fixed carbon, per cent.....	54	.....	.....	59.5
Poles, kinds, no. per charge.....	Hard wood 15	.....	.....	Beech, maple 3500 lb. Hard wood 680 lb.
Charcoal, kind, lb. per charge.....	2000	.....	.....	.....
Labor, in 24 hr.....	14	.....	.....	.....
Copper produced, character.....	Cake, ingot	Cake, ingot, anode	.....	Ingot, cake, bar, anode
Copper, per cent. of charge.....	60	50 ±	.....	90
Copper, manner of casting.....	Walker machine	Hand	.....	Bull-ladle
Slag, SiO <sub>2</sub> .....	46	.....	.....	21.3
Fe(MnO)O.....	17	.....	.....	15.3
Al <sub>2</sub> O <sub>3</sub> .....	12	.....	.....	8.4
CaO.....	10	.....	.....	5.9
Cu.....	7	.....	.....	43.4
Slag, per cent. of charge.....	45	.....	.....	15
Slag, disposition.....	Blast-furnace	.....	.....	Part to rever- beratory, mostly to blast-furnace

Two furnaces, shown in Figs. 388-391 and 393-395, may serve as examples of the old and modern types. The furnace, Figs. 388-391, is the one formerly used by Park Brothers & Co., Pittsburgh, Pa.<sup>1</sup> The drawings with legend require little discussion. The sand-bottom, *i*, is burnt in on the inverted arch, *i'*; the crown of the latter rests upon the arch, *j*, built up from the foundations; the space between the arches is filled with slag and mill tailings. The furnace is run with undergrate blast delivered to the central underground flue; the blast strikes in the ashpit a hinged deflecting-plate which forces part of the under-wind to pass through the upturned ports in the hollow bridge-wall. This furnace, 12 ft. 10 in. long by 9 ft. 9 in. wide, used to receive a charge of 7 tons of mineral to be worked in 24 hr.

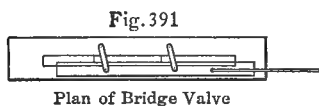
The furnaces in operation at present are larger, holding from 25 to 35 tons of copper; further, the former sand-bottom has been replaced in a few instances by two courses of silica-brick laid in the form of an inverted arch, with about

<sup>1</sup> Egleston, *Tr. A. I. M. E.*, 1880-81, IX, 678.

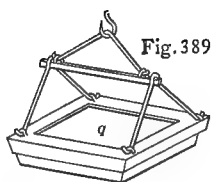
Johns, *Eng. Min. J.*, 1912, XCIII, 1183, history.



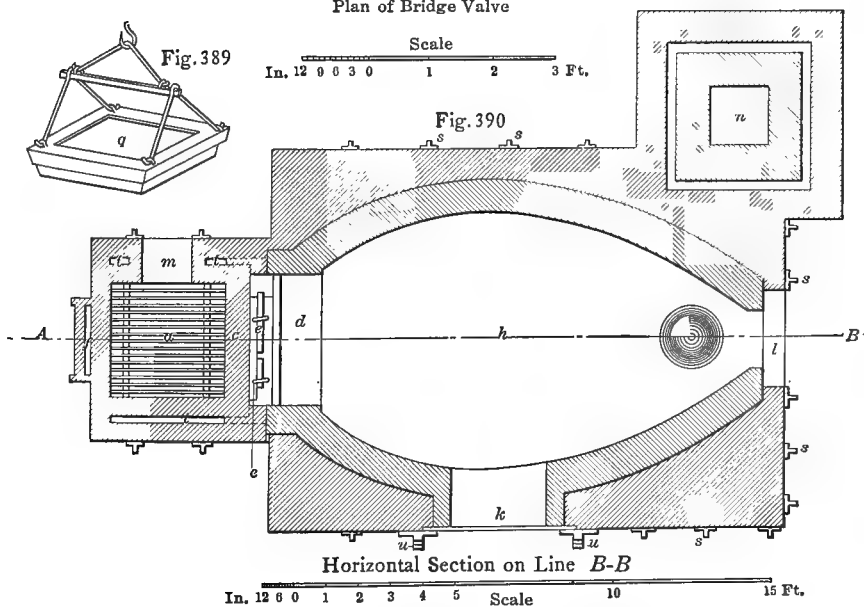
Vertical Longitudinal Section on Line A-A



Plan of Bridge Valve



Scale  
In. 12 0 0 1 2 3 Ft.



Horizontal Section on Line B-B

- |   |                                     |  |
|---|-------------------------------------|--|
| <i>a</i> Fire place   | <i>h</i> Laboratory of the furnace  | <i>n</i> Chimney 53 feet high  |
| <i>b</i> Ash pit  | <i>i</i> Sand bottom                | <i>o</i> Flue to <i>n</i>  |
| <i>c</i> Bridge wall  | <i>j</i> Mortared brick arch        | <i>p</i> Movable roof  |
| <i>d</i> Right air passage 1.5 x 3 in. controlled by valve <i>e</i> | <i>k</i> Arch supporting the hearth | <i>q</i> Cast Iron T bars holding furnace together                     |
| <i>e</i> Bridge valve   | <i>l</i> Charging door              | <i>r</i> Air passages leading to <i>d</i> for support of tool and pole |
| <i>f</i> Air passage controlled by the valve <i>g</i>               | <i>m</i> Working door               | <i>u</i> Sockets for bars  |
| <i>g</i> Roof valve   | <i>m</i> Fire door                  |  |

FIGS. 388 TO 391.—Reverberatory furnace for Lake Superior copper ore.





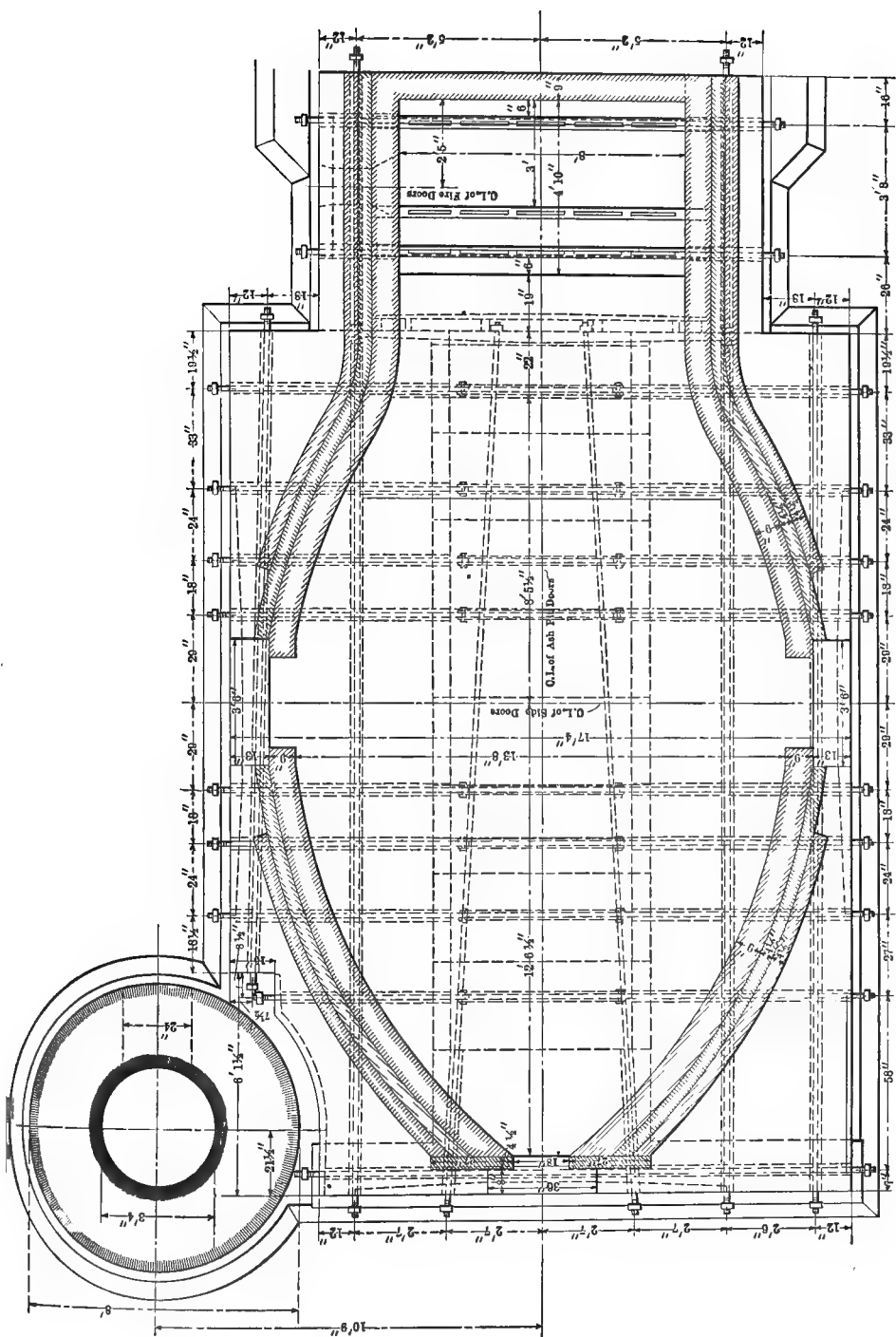


FIG. 394.—Reverberatory furnace, Calumet & Hecla Mining Co., Buffalo, N. Y.

ground chamber running along the median line, while the rest is carried by a concrete foundation. The hearth, 21 ft. by 13 ft. 8 in., has a silica-brick floor on which is the burnt-in sand-bottom. The sides are silica-brick backed by two  $4\frac{1}{2}$ -in. courses of fire-brick; the roof is of silica-brick; an inclined flue leads the gases to a circular brick stack. Of special interest are the tie-rods which bind together the sides. They pass through the side and foundation walls in inclined steel pipes and are connected in the longitudinal chamber by short horizontal rods; the rods, some distance from the hotter part of the furnace, are air-cooled, as is the case with the longitudinal tie-rods taking up the end-thrust

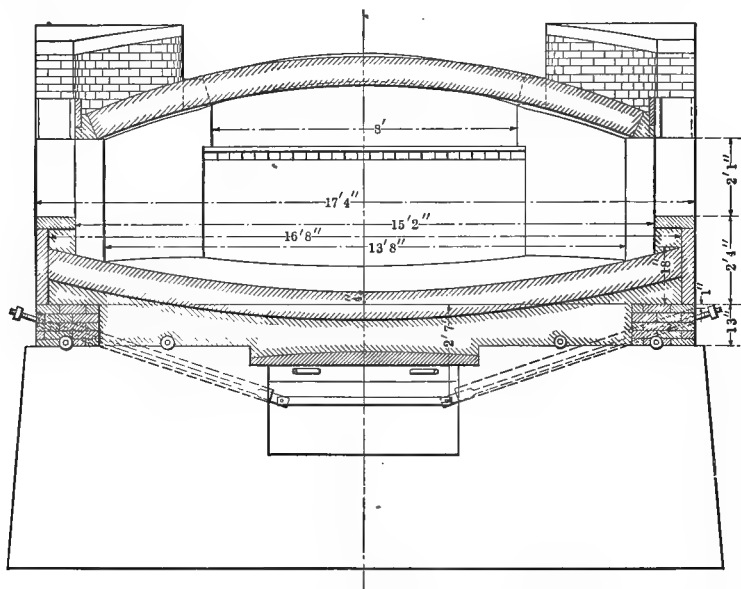


FIG. 395.—Reverberatory furnace Calumet & Hecla Mining Co., Buffalo, N. Y.

of the furnace, by air passing through the pipes. The fire-box and roof have the usual air-ports. The 4-ft. bars of the rocking grate run parallel with the length of the furnace; the outer wall of the fire-box rests on a cast-iron plate supported by cast-iron columns, thus leaving open the ashpit below.

**184. Mode of Operating.**—The mode of operating, which includes the six operations of charging, melting and skimming, fining or rabbling, poling or refining, ladling or casting, and repairing is similar to that of refining black or blister copper to be taken up in detail in §186. Only a brief outline will be given here.

At most of the works the entire process is carried on in the same reverberatory furnace, and the time given to a charge is about 24 hr.: charging, melting and skimming, 14–16 hr.; fining (rabbling) 1–2 hr.; poling (refining) 2 hr.; ladling (casting) and repairing, 4–5 hr. The casting is intended to be begun with the arrival of the day shift.

At the Michigan smelter<sup>1</sup> melting and skimming are carried on in two melting furnaces with shallow hearths, 35×16 ft., each of which treats in 24 hr. from 60 to 80 tons of charge, according to the character of the material. As fast as the slag is formed and has accumulated in quantities of about 5000 lb., it is skimmed into a set of five molds resting on a car. When the full charge for a furnace has been smelted, the slag is skimmed off, and the metal tapped into an adjoining refining furnace, placed 7 ft. below, with deep hearth, 23 ft. 3 in. by 14 ft. 4 in. As this process does not require 24 hr. to finish the molten copper, it is charged with from 10 to 15 tons of mass or barrel work which is melted down in time for the furnace to receive the liquid copper from its melting furnace. At the Buffalo works of the Calumet & Hecla Mining Co., a similar proceeding is in operation with No. 1 mineral which assays Cu 70 per cent. and passes for the greater part through a 40-mesh sieve.

The melting furnace is fired and charged with mineral to which 1.5 per cent. limestone has been added as flux. When the first charge is melted, more charge is given, and the slag skimmed when necessary. This is continued until the furnace is filled with copper, and then its content tapped into a refining furnace, where the metal is brought to tough-pitch and cast with a Walker machine (§ 194) into ingots and ingot-bars.

The question of keeping melting and refining separate is governed mainly by the size of the charge to be treated. With charges of 20 to 35 tons there is no reason for keeping apart the two operations, as the depth of the hearth is not so great as to prevent the smelting from being efficient. With a charge of 150 tons, where the hearth must be about 3 ft. deep, the smelting efficiency would be very low, as the mineral lying on the bottom would not be exposed to a greater heat than the temperature of the molten copper floating above, and the formation temperature of the slag is higher than that of the molten copper. Both causes make it extremely difficult for the mineral to reach the hot zone of the furnace.

In ordinary practice the coarser concentrate to be charged into a furnace is drawn from draining storage-bins, either into 1- or 2-ton cars and brought to the hoppers in the roof of the furnace, or on to a conveyor which delivers into the hoppers.

In starting a furnace, the working-bottom of the hearth is covered with concentrate, then follows coarse copper, such as mass, or barrel work, headers fed through the side doors; the rest of the charge is dropped through the hopper in the roof. The charge may receive as much as 8 per cent. limestone as flux; frequently it is covered with rich refinery slag. The doors are closed and luted, and the fire is urged. The charge melts down gradually in about 16 hr.; slag is skimmed as fast as it is formed. During the melting most of the Fe present is scorified. The fining (rabbling) was formerly done by hand (flapping) with a rabble (head 4×6 in., handle 8 ft. long). At present it is accomplished

<sup>1</sup> White, *Eng. Min. J.*, 1905, LXXIX, 842.

Austin, *op. cit.*, 1906, LXXXI, 83.

better and more quickly by compressed air of 16–20 lb. pressure passing through two or four  $\frac{3}{4}$ -in. pipes thrust downward into the metal through the side doors. The slags rising to the surface are skimmed, and oxidation is continued until the stage of set copper (Cu with about 6 per cent.  $\text{Cu}_2\text{O}$ ) is reached. It is important that the dip sample (button) show a smooth concave surface, and the fracture a single bubble under the depression. The  $\text{Cu}_2\text{O}$  is now reduced by poling with poles of hard (poplar) wood 18–24 ft. long and 6–8 in. in diameter at the butt end, thrust into the copper through the front door. When the poling is well advanced, the surface of all or only of part of the metal is covered with charcoal to prevent oxidation. Poling is continued until the hemispherical button-sample, 2 in. in diameter and  $\frac{3}{4}$  in. thick, shows a level, smooth or wrinkled surface, and the fracture a rose color and a silky luster. From 8 to 12 poles are used up in the  $1\frac{1}{2}$ –2 hr. it takes to pole a charge. The copper is now cast by dipping with small hand-ladles, or with large swinging (bull-) ladles, or by a casting machine (endless chain, or Walker) through a trolley- or dipping-ladle, into ingots (20 lb.), bars (60–90 lb.), round or square cakes (100–1000+ lb.), anodes ( $250 \pm$  lb.).

Electric conductivity tests are made on ingot, bar, and cake copper. The furnace is fettled after every cast; it has to be repaired about every eight weeks; the roof lasts about eight months, the fire-box about four months.

Slime concentrate which is too fine, and usually too impure, to go into the reverberatory furnace with coarse ore, is charged into a special reverberatory furnace with cupola copper, refined and cast into anodes, or it is agglomerated in a reverberatory furnace, or briquetted.

The agglomeration is carried on on a bath of cupola copper. The fine material is piled on the bath from the hopper in the roof and melted down gradually. The sides of the conical heap become glazed, the slag formed trickles down and is skimmed as fast as it is formed. When the cone of fines has diminished somewhat in size, new material is fed into the hopper by means of a belt elevator. Thus the process of agglomerating is continuous. The slag contains about 17 per cent. Cu and goes to the blast-furnace; part of the accumulated copper, forming about 25 per cent. of the ore, is tapped at intervals, and then worked with cupola copper.

In briquetting, lime is used as a bond. The White briquetting machine<sup>1</sup> furnishes the well-known small cylindrical briquettes. They are piled on iron cars, placed in a cylinder, and steamed as is the case in the manufacture of lime-sand brick.<sup>2</sup> The hardness of the briquettes is sufficient to make them suited for blast-furnace work.

**185. Blast furnace.**—Some data of the blast-furnace work of the Michigan and the Calumet and Hecla smelteries are given in Table 92.

<sup>1</sup> Hofman, "General Metallurgy," 1913, p. 638.

<sup>2</sup> Eckel, E. C., "Cements, Limes and Plasters," Wiley, New York, 1905, pp. 130–147.

TABLE. 92—BLAST-FURNACES FOR SMELTING NATIVE COPPER ORES AND BY-PRODUCTS

	Michigan Smelting Co.	Calumet & Hecla	
		Hubbel	Buffalo
Horizontal section at throat	4' 9" × 12'		5' × 7' 6"
Area at throat, sq. ft.	57		37.5
Horizontal section at tuyères	3' 4" × 12'	3' 6" × 12'	2' 9" × 7' 2"
Area at tuyères, sq. ft.	39.9	40	19.85
Height, tuyères to throat	7' 6"	7' 3"	8' 0"
Height, tuyères to top of crucible	0' 7"	0' 7.5"	1' 3"
Water-jackets, height	6' 10½"	10' 1½"	5' 2"
Bosh, height	6' 10½"		
Bosh, amount inches in ft.	9.5" in 6' 10.5"		
Crucible, depth	1' 9½"	2' 2"	1' 0"
Forehearth, fixed or movable	Fixed	Fixed	Two movable
Forehearth, shell dimensions	4' × 6'	Two 3' × 6' and 3' 6" deep	3' × 5' and 4' deep
Tuyères, number	18	24	18
Tuyères, diameter	4"		4.5"
Tuyère-ratio	5.92:1	7.53:1	4.58:1
Charge (ore, + flux) weight, lb.	6000		2780
Charge, tons in 24 hr.	200		160
Charge, tons per sq. ft. hearth area in 24 hr.	5		
Cu, per cent. of charge	20		
Coke, per cent. of charge	6		
Coke, per cent. ash	11		
Anthracite, per cent. of charge	6½		16.6
Anthracite, per cent. ash	14		7
Blast, cu. ft. per min.	6000		6000
Blast, pressure oz.	4		18
Cooling water for jackets, gal. per hr.			9000
Granulating water, gal. per ton slag			
Men, number in 24 hr., a (regular crew) + b (accessory labor)	15		
Slag, SiO <sub>2</sub>	40		30.8
Fe(Mn)O	17		24.3
Ca(Mg)O	20		31.7
Al <sub>2</sub> O <sub>3</sub>	15		12.1
Cu	0.9		0.64
Specific gravity	3.4		3.362

The blast-furnaces, formerly circular or elliptical in horizontal section, are all rectangular and have internal crucibles. The charge consists of reverberatory slag, briquettes, siliceous or ferruginous flux, limestone, and a mixture of anthracite and coke. The reverberatory slag from amygdaloid mineral is acid (SiO<sub>2</sub> 40, FeO 20 per cent.); that from conglomerate basic (SiO<sub>2</sub> 25, FeO 45 per cent.). If the slag belongs to different mining companies, it has to be smelted separately, as the irregularity of the copper-content makes sampling impracticable. The normal blast pressure of about 16 oz. has been reduced in some instances to 4 oz. to insure a better reduction through slower smelting, 240 tons of charge *vs.* 70 tons. The black copper, with 95+ per cent. Cu and some S from the fuel, is tapped at fixed intervals; the slag overflows continuously through a trapped spout either into a single large brick forehearth, or into two smaller ones placed in series, from which settled copper is tapped at long intervals. The waste slag with 0.75 per cent. Cu is collected in pots or granulated.

The cost of smelting in 1906 at the works of the Lake Superior Mining Co., treating 41,176 tons of mineral, was \$7.293 per ton of ore.<sup>1</sup>

<sup>1</sup> Austin, *Min. Sc. Press*, 1909, xcviii, 592.

D. FIRE-REFINING OF IMPURE COPPER<sup>1</sup>

**186. Introductory.**—In smelting copper ore in the blast- or reverberatory-furnace, and copper matte in the converter, there are obtained black copper, blister copper, and coarse or converter copper, all of which contain impurities which make the metal unfit for industrial use. These impurities may be Fe, Pb, Zn, Sn, Co, Ni, As, Sb, Bi, S, Se and Te; further Ag, Au, Cu<sub>2</sub>O and gases. The aim of refining is to remove the impurities as much as possible, and to produce a copper of a required purity having the necessary mechanical properties and electric conductivity. The process of fire-refining consists in an oxidizing fusion in order to volatilize some metals and to oxidize and scorify others which have a greater affinity for O than has Cu, followed by a reducing fusion in which most of the Cu<sub>2</sub>O formed and held in solution by the copper is reduced to Cu. A small amount of Cu<sub>2</sub>O ( $0.5 \pm$  per cent.) is always left in the Cu in order to insure the presence of any remaining impurity in the state of oxide in which it is less harmful than if in that of metal, when it is likely to form a solid solution.

**187. Furnace.**—Formerly the process was carried out in hearth-furnaces,<sup>2</sup> from which the copper was obtained in the form of round discs as so-called "rosette-copper." In recent years the electric furnace has been suggested<sup>3</sup> for refining, but it has not yet come into practical use. The only furnace that need be considered is the reverberatory furnace. The general statements regarding this furnace for the smelting of native copper ore (§ 183) hold good for the refining of copper. The main difference is that of size of furnace, which is caused by the form and character of the material to be treated, and with it that of the manner of charging and discharging. A refining furnace may have to work cakes of low-grade black copper and high-grade blister copper, sheets of pure cathode copper, or liquid converter copper. If the copper be low grade and require a prolonged refining operation,<sup>4</sup> the furnace will have to be small, probably not exceeding 20 tons capacity; if the copper be nearly pure, the capacity may be very much increased, reaching 100, 150, and even 250

<sup>1</sup> Stetefeldt, *Berg. Hüttenm. Z.*, 1863, XXII, 185, 205, 219.

Hampe, *Zt. Berg. Hütten. Salin. Wesen i. P.*, 1873, XXI, 218; 1874, XXII, 93.

Egleston, *Tr. A. I. M. E.*, 1880-81, IX, 678.

Stahl, "Dissertation," 1886; *Metallurgie*, 1907, IV, 761.

Keller, *Min. Ind.*, 1898, VII, 245; *Tr. A. I. M. E.*, 1898, XXVIII, 137; 1900, XXX, 310.

Gibb, *op. cit.*, 1903, XXXIII, 661.

Hofman-Green-Yerxa, *op. cit.*, 1904, XXXIV, 671.

Hofman-Hayden-Hallowell, *op. cit.*, 1907, XXXVIII, 171.

Wanjukow-Schmidt, *Metallurgie*, 1909, VI, 749.

Johnson, *Met. Chem. Eng.*, 1911, IX, 396.

Emrich, *Tr. A. I. M. E.*, 1912, XLIII, 446.

Peters, E. D., "Practice of Copper Smeltery," McGraw-Hill Book Co., New York, 1911, pp. 531-547.

<sup>2</sup> Percy, J., "Metallurgy," Murray, London, 1861, pp. 399, 406.

Schnabel, C.-Louis, H., "Handbook of Metallurgy, Macmillan, New York, 1905, I, 248.

<sup>3</sup> Rauschenplatt, *Metallurgie*, 1910, VII, 151, 435 (Borchers).

<sup>4</sup> Platten, *J. Soc. Chem. Ind.*, 1906, XXV, 449.

tons.<sup>1</sup> The reduction in fuel-consumption by this increase in capacity is shown by the curves of Keller<sup>2</sup> and Peters<sup>3</sup> given in Fig. 396. The curve of Peters shows that the saving in fuel is small when the charge is greater than 50 tons.

The bottom of the furnace and the manner of its support, as well as the construction of the sides of the furnace, have received much consideration with the increase of the weight of the charges. The bottom used to be built up exclusively of sand burnt in, as is still the common practice with matting furnaces (§139). In a few instances silica-brick have replaced the sand-bottom, as has been done with some matting furnaces and in the furnace of the Michigan smelter, Fig. 392. With some furnaces the cooling vault, given up in matting furnaces, has been retained; with others the hearth has been built on cast-iron plates supported by brick pillars. The reason for air-cooling the bottom<sup>4</sup> is

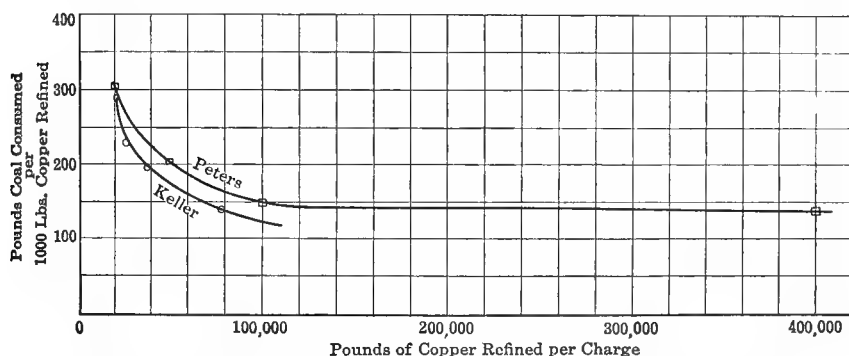


FIG. 396.—Relation between coal consumption and size of refining charge.

that in melting large charges of metallic copper there is danger of the hearth becoming too hot and breaking out; hence the additional cooling with increase of weight of charge. With furnaces holding 200 and 250 tons metal<sup>5</sup> there has arisen the difficulty of making the bottom sufficiently strong so that it will not come up. This has been overcome by a forced circulation of air through a series of 2½- or 3-in. pipes, running crosswise underneath the brickwork carrying the sand-bottom, and joined at the ends to two longitudinal pipes, one of which is connected with a fan, while the other is extended into the ashpit of the fire-place. With a 225-ton furnace 100 pipes receive 5000 cu. ft. air per minute. This forced ventilation with a foundation built up solid is believed to be preferable to natural ventilation with a hearth resting upon cast-iron plates supported by brick pillars.

<sup>1</sup> Addicks, *Eng. Min. J.*, 1907, LXXXIII, 1002.

Prosser, *op. cit.*, 1907, LXXXIV, 171.

Walker, *Min. Ind.*, 1910, XIX, 221.

<sup>2</sup> *Min. Ind.*, 1898, VII, 250.

<sup>3</sup> Practice of Copper Smelting, 1911, p. 567.

<sup>4</sup> *Eng. Min. J.*, 1913, XCV, 576 (Herreshoff), 816 (Cloud), 864 (Nason).

<sup>5</sup> Walker, *Min. Ind.*, 1910, XIX, 221.

The inner sides of a furnace have been recently constructed in part of magnesite brick instead of silica-brick throughout as before, as they appear to stand better the corrosive effect of the charge. The magnesite brick reach from below the silica bottom to a short distance above the highest level of the metal bath.

The roof is always made of silica-brick. The contact planes between magnesite and silica-brick are formed by a course or two of neutral chrome brick. The latest innovation is that of Addicks and Brower<sup>1</sup> who have in operation at Chrome, N. J., a refining furnace with bottom of magnesite brick, and sides and roof of chrome brick.

The hearth of a refining furnace has to be seasoned with copper as has that of a matting furnace with matte (§ 139). The bottom is covered with a few inches of copper; this is melted slowly and gradually absorbed. The temperature is slightly lowered, and a second portion of metal charged, melted, and absorbed. The operations are repeated until all the copper that will be absorbed has been taken up. Some of the Cu will be oxidized to  $\text{Cu}_2\text{O}$  and slagged by the  $\text{SiO}_2$ ; the slag formed acting as a cementing material strengthens the bottom. A sand-bottom absorbs more copper than does one built of silica-brick; a furnace resting upon plates locks up less copper than one supported by a solid or even a vaulted bottom. It is essential that the copper used for seasoning be of a high grade so as not to "poison" the metal to be refined. An interesting case of such poisoning was that of Baltimore where Te was the harmful metal.<sup>2</sup>

A small furnace will be charged by hand and the copper cast with hand-lasses, a large furnace requires mechanical charging and molding by means of a casting machine.

The air necessary for fining may be admitted through ports in the fire-bridge, or blown in through tuyère-pipes placed on either side of the fire-bridge.

The fuel may be bituminous coal, oil residuum, or producer gas. The waste heat of the furnace may be recovered in part by recuperation or regeneration; in recent years the gases of most furnaces have been conducted through waste-heat boilers.

All operations are usually so conducted that it takes 24 hr. to work a charge.

The furnaces of the Anaconda Copper Mining Co. at Great Falls, Mont., Figs. 397-399, the Balbach S. & R. Co., Newark, N. J., Figs. 400-404, and the United States Metals Refining Co., Figs. 405-410, may serve as examples of modern refining furnaces. Their leading dimensions and their work as well as similar data of other furnaces are assembled in Table 93.

Descriptions of some refining plants given in the technical literature are those of the First Raritan Works,<sup>3</sup> United States Metals Refining Co.,<sup>4</sup> Rio Tinto works,<sup>5</sup> and the Second Raritan Works.<sup>6</sup>

<sup>1</sup> *Eng. Min. J.*, 1914, XCVII, 421.

<sup>2</sup> Egleston, *Tr. A. I. M. E.*, 1882, x, 493.

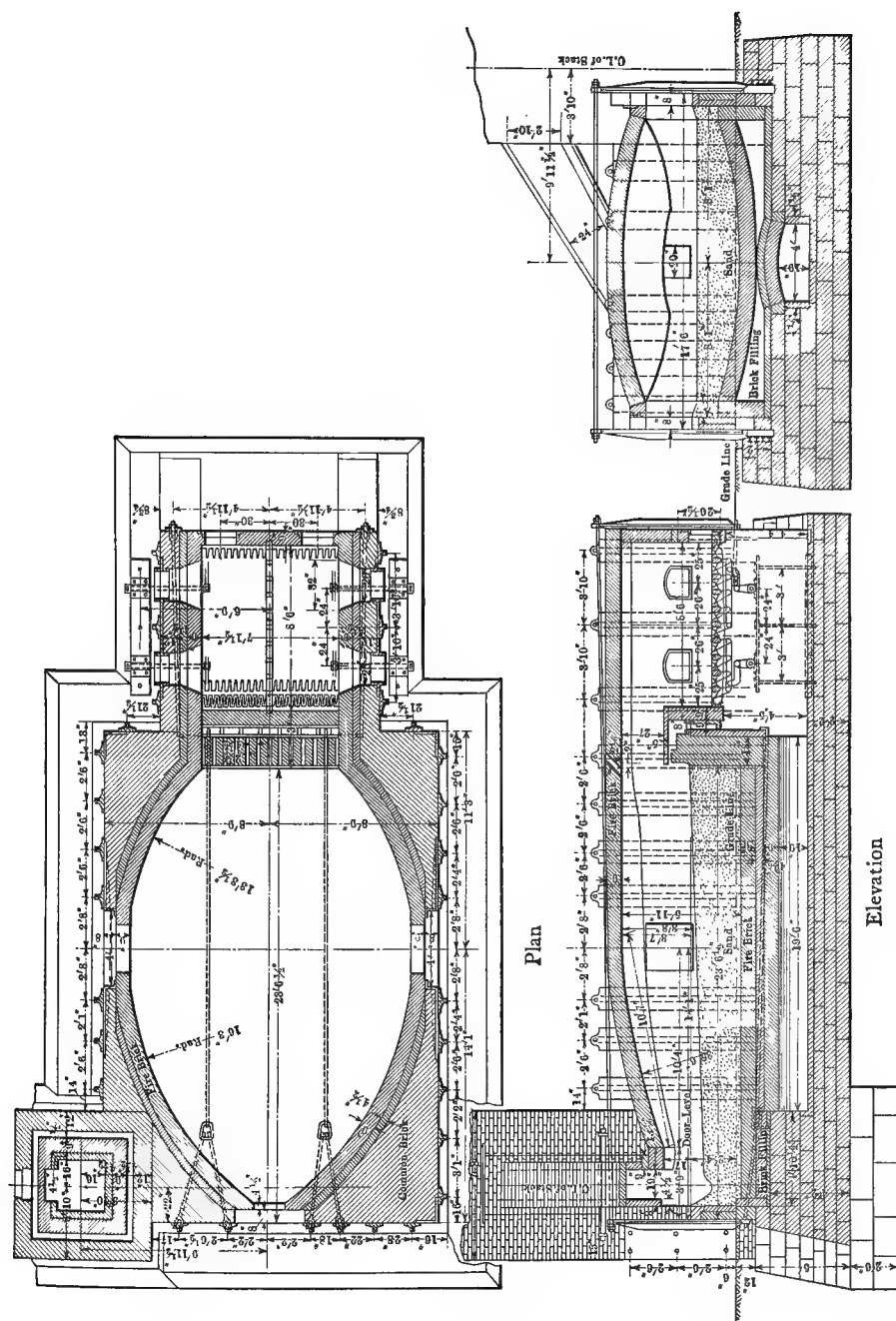
<sup>3</sup> Addicks, *Min. Ind.*, 1900, ix, 261.

<sup>4</sup> Addicks, *Min. Ind.*, 1906, xv, 301; *Eng. Min. J.*, 1907, LXXXIII, 1001.

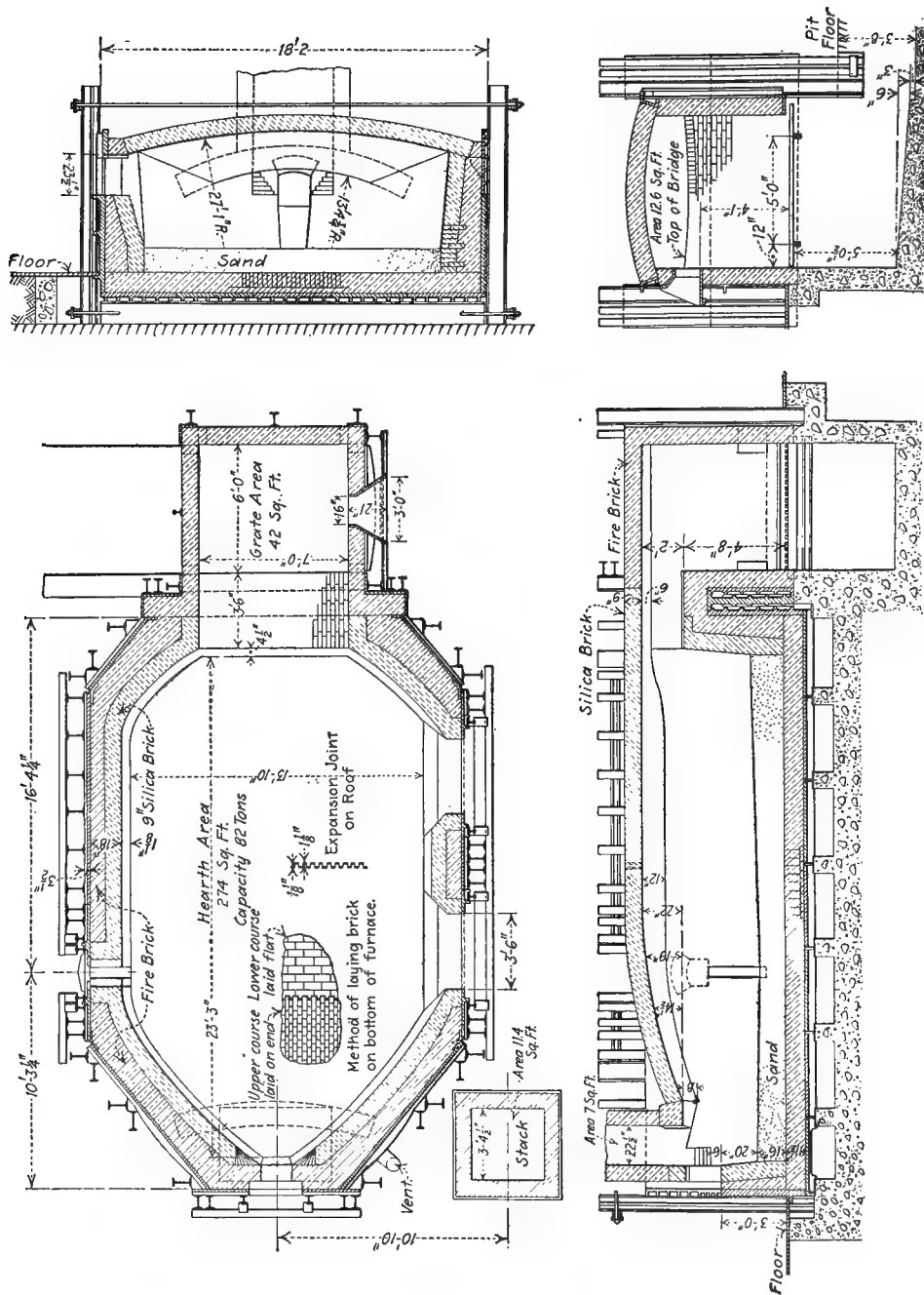
<sup>5</sup> Walker, *Eng. Min. J.*, 1907, LXXXIV, 111.

<sup>6</sup> Easterbrooks, *Electrochem. Met. Ind.*, 1908, vi, 245.





FIGS. 397-399.—Copper refining furnace, Great Falls, Mont.



FIGS. 400-404.—Copper refining furnace, Balbach Smelting &amp; Refining Co., Newark, N. J.

The furnace of the Anaconda Copper Mining Co., Great Falls, Mont., shown in Figs. 397-399, serves for the refining of cathodes.<sup>1</sup> Its capacity is 35 tons of cathodes or 62 tons of fluid converter metal. The hearth, 23 ft. 6½ in. × 15 ft., has the pear-shaped form characteristic of the original Welsh furnace. It has the form of an inverted arch and rests on the center line of a segment arch covering a central cooling chamber. The dish-shaped sand-bottom slopes 9 in. from fire-bridge to flue, where is situated the depression necessary to receive the suspended bull-ladle, 14-19 in. in diameter, for casting ingots, cakes, or wire-bars. There is a single working door on either side, and a rabbling and ladling door beneath the inclined flue; the roof, of silica-brick, is horizontal for half the length of the hearth to allow for free development of flame, and then only pitches downward toward the flue. Air for oxidation is admitted through ports in the roof and the fire-bridge. The grate-area is large when compared with that of the hearth area, viz., 1:3.7; the cast-iron grates are provided with mechanical shakers; the coal is fed through two doors placed on either side.

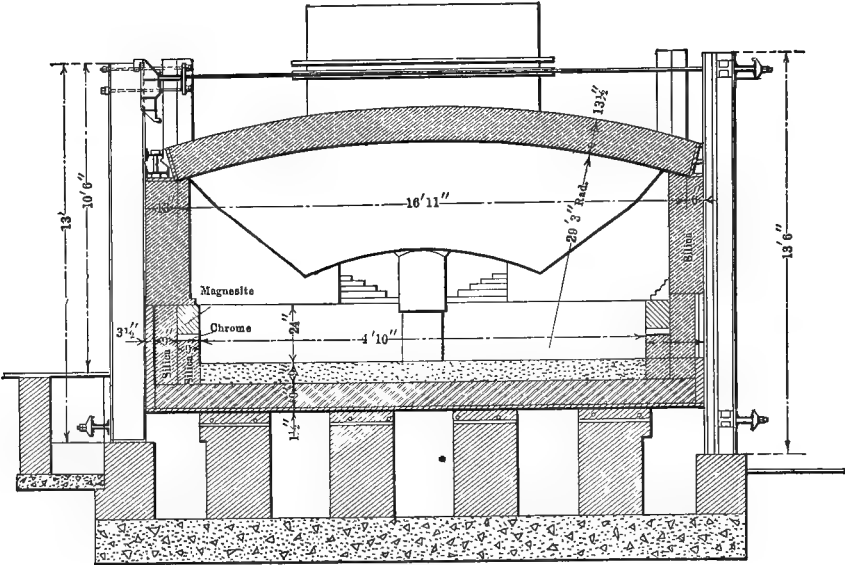
The furnace of the Balbach Smelting & Refining Co., Newark, N. J., shown in Figs. 400-404, also serves for the refining of cathodes. Its capacity is 80 tons of copper. The hearth, 23 ft. 3 in. × 13 ft. 10 in., has straight sides and curved ends; it is carried by heavy ribbed cast-iron plates supported by brick pillars; the open space is cooled by forced draft. The sand-bottom slopes from fire- and flue-bridges toward the tap-hole placed in the side toward the flue-end. There are two working doors on the side opposite the tap-hole, and a rabbling door at the flue-end. The roof of silica-brick, has an expansion joint 1½ in. wide. The grate area is relatively small, presupposing the use of a good grade of coal; the grate bars are wrought iron; there is a single fire-door.

The furnace of the United States Metals Refining Co., Chrome, N. J., shown in Figs. 405-410, also a cathode furnace, has a capacity of 250 tons of copper. The hearth, 33 ft. 8 in. × 14 ft. 10 in., has straight sides; the fire-bridge end is not curved; the flue-end is contracted as usual. The hearth consists of a full course of fire-brick on which is burnt in a mixture of sand and rolling-mill scale to serve as working-bottom; the brick rest on cast-iron plates which are supported by red-brick pillars. The hearth slopes from fire- and flue-bridges to the tap-hole placed in the side toward the flue-end. The sides are built of silica- and magnesite brick, the two are separated by a course of neutral chrome brick. There are three charging doors in the side opposite the tap-hole, and the usual rabbling and skimming door at the flue-end. The long horizontal part of the silica-brick roof is separated by one expansion joint, 1½ in. wide, from the short pitching part leading to the flue, and by another, also 1½ in. wide, from the roof of the fire-box. The wrought-iron grate bars, 1½ in. square, have a 3-in. pitch; there are two fire-doors on one side.

Peters<sup>2</sup> describes a gas-fired refining furnace with regenerators having a

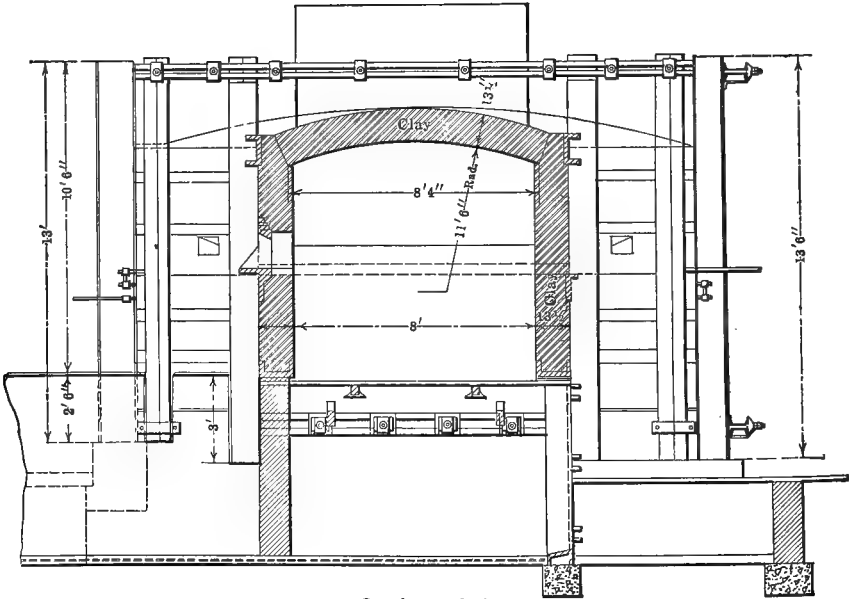
<sup>1</sup> Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 313.

<sup>2</sup> "Modern Copper Smelting," 1895, p. 575.



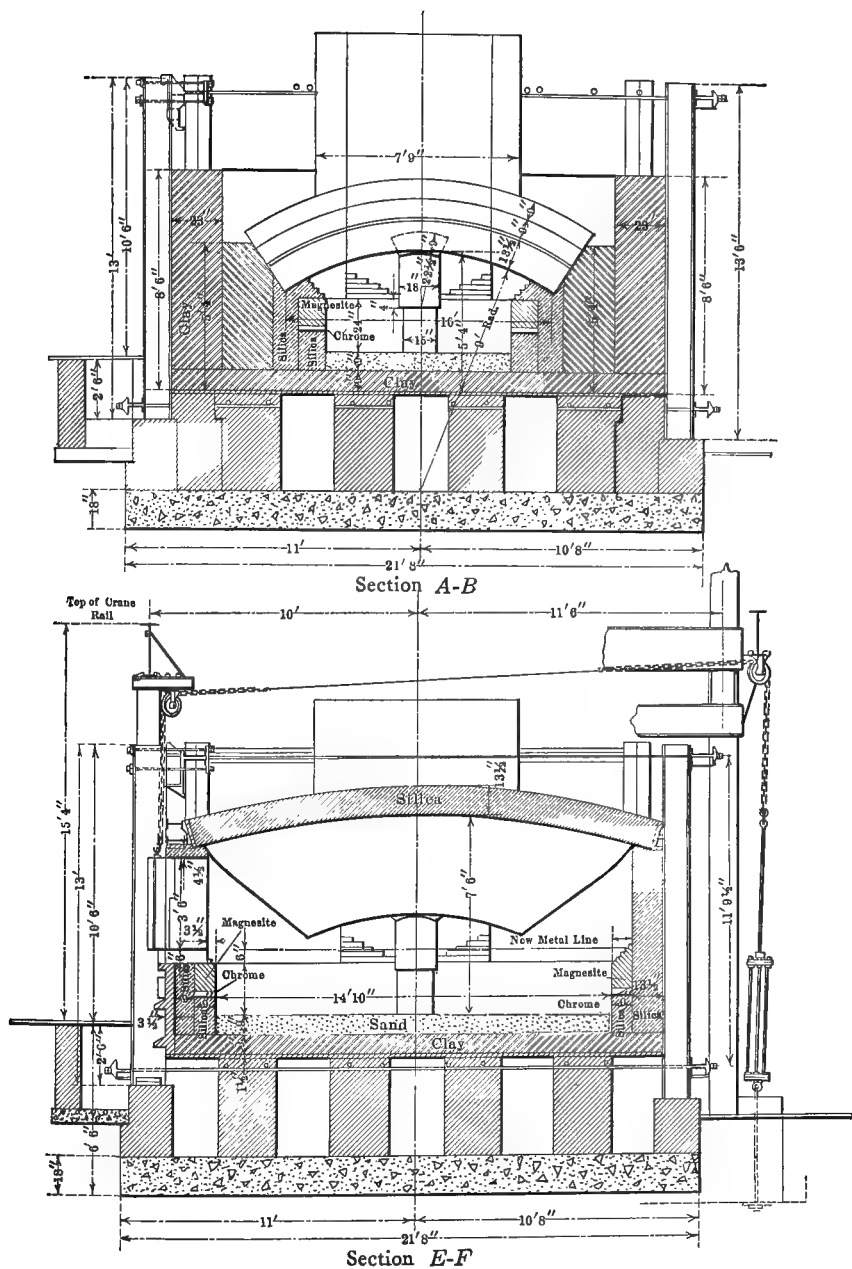
Section C-D

FIG. 405.—Copper refining furnace, United States Metals Refining Co., Chrome, N. J.

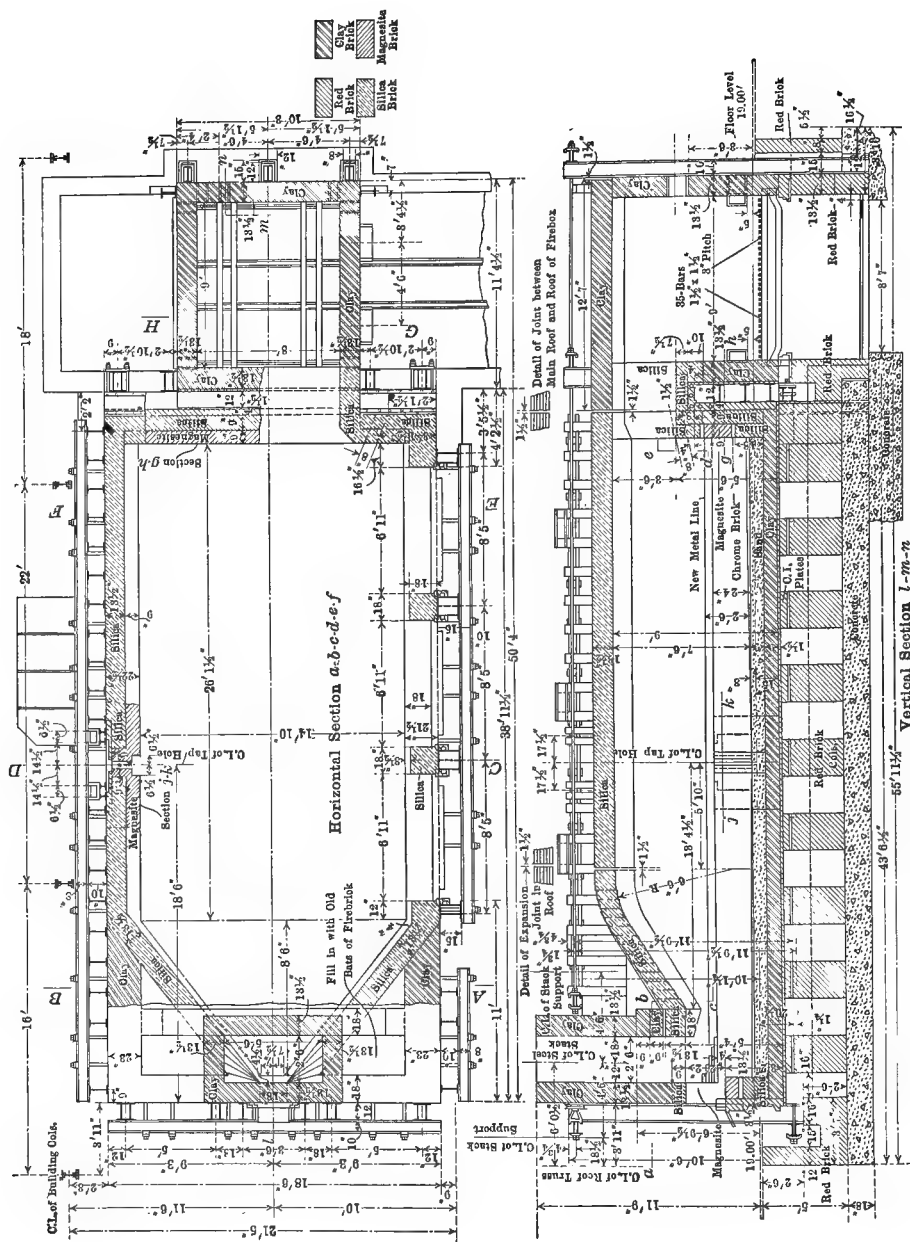


Section G-H

FIG. 406.—Copper refining furnace, United States Metals Refining Co., Chrome, N. J.



FIGS. 407-408.—Copper refining furnace, United States Metals Refining Co., Chrome, N. J.



FIGS. 409-410.—Copper refining furnace, United States Metals Refining Co., Chrome, N. J.

capacity of 5000 lb. copper. Steck<sup>1</sup> suggests a tilting gas-fired furnace with regenerators and converting-tuyères.

**188. Mode of Operating in General.**—The operations carried on in refining are charging, melting, fining (rabbling), dense-poling, tough-poling, and ladling or casting. These will be taken up in order, and followed by records of refining impure black copper and pure cathode copper.

**189. Charging.**—In charging solid copper, the cakes used to be, and frequently still are, placed by hand on a paddle, slid into the furnace, and deposited in such a manner as to allow the fire-gases to come as much as possible into contact with the individual pieces. Thus about 8 tons may be charged per hour through one door. With the increasing sizes of the furnaces the speed of charging had to be accelerated. By raising the material to be charged<sup>2</sup> with air-lifts (pneumatic pistons, with tongs, running on a traveler) on to the paddles, the rate of charging has been increased to from 17 to 20 tons per hour per door, or a 35- to 40-ton furnace can be charged from the usual two doors in 1 hr. by a crew of 10 men. A crew of 12 men (2 air-lifts with 6 men, 2 paddles with 6 men) will charge through two doors 150 tons of blister copper in 3 hr. Charging a 200-ton furnace through 3 doors, unduly prolongs the operation; 4 or 6 charging doors, which would shorten the time, are inconvenient. Electrically driven mechanical charges for cathodes have been constructed by Prosser and Ladd,<sup>3</sup> Addicks,<sup>4</sup> and Clark-Antisell,<sup>5</sup> by means of which 150 tons of cathodes are charged in less than 2 hr. by 2 men. Thus one of the difficulties which limited the size of a furnace has been overcome. With such bulky material as cathode copper the whole charge cannot be introduced at once; hence about three-fourths is charged at first, and, when melted down in part, followed by the remainder. Thus with a 200-ton furnace, 150 tons will be charged in from 1½ to 1¾ hr., melted down in part in about 4 hr., and then 50 tons more added. In order to protect cathodes against the sulphurous gases of the coal used at Great Falls, they are dipped into milk of lime<sup>6</sup> after they have been freed from adhering electrolyte by washing with water.

With liquid converter copper, the content of the converter is poured into a ladle and then through a movable brick-lined spout into the refining furnace. At Anaconda,<sup>7</sup> e.g., 5-ton steel ladles, plastered with finely ground ore to a thickness of 4 in. and manipulated by an overhead electric traveling crane deliver the metal to two refining furnaces<sup>8</sup> (Table 93) of 100 tons capacity. The charge is made up of 90–95 tons of liquid converter copper and 6–7 tons of scrap (ladle sculls, defective anodes, etc.). It takes 1–2 hr. to charge scrap, 8 hr. to charge converter metal; fining by blowing in air under 15 lb. pressure begins when the

<sup>1</sup> *Feuerungstechnik*, 1913, I, 213; *Metall-Erz*, 1913, X, 499.

<sup>2</sup> Prosser, *Eng. Min. J.*, 1907, LXXXIV, 171.

<sup>3</sup> *Eng. Min. J.*, 1908, LXXXVI, 867.

<sup>4</sup> *Min. Ind.*, 1906, XV, 304.

<sup>5</sup> *Eng. Min. J.*, 1910, XC, 264.

<sup>6</sup> Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 313.

<sup>7</sup> Austin, *Tr. A. I. M. E.*, 1906, XXXVII, 431.

<sup>8</sup> Drawing in Peters "Practice of Copper Smelting," 1911, p. 571.

furnace is two-thirds filled, and in finished when the furnace has received its entire charge. The copper is then poled for 2 hr. and cast into anodes at the rate of 25 tons per hour.

**190. Melting.**—When the furnace is charged, the side doors are closed, luted, the fire-box is filled with coal, and the fire urged to cause the fusion of the copper. Impure black copper will be melted down slowly, and air admitted through the ports in order to assist the oxidation and elimination of foreign metals; toward the end of a melt blast may be turned on. Pure blister or cathode copper is melted quickly and with closed air-ports, as all oxidation necessary can be readily accomplished during the fining period. In from 8 to 12 hr. after charging, the copper will be fused and covered with a layer of slag made up of slagable impurities, mainly Fe, perhaps some Sn, Zn, Co, Ni, Pb, then  $\text{Cu}_2\text{O}$  and  $\text{SiO}_2$ , some  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and of shots of Cu. The slag is skimmed. A sample of impure black copper will show a raised rough surface, and the section a dark red color and blisters. The fracture of a high-grade blister copper sometimes has a radiated and columnar structure.

The grate is now cleaned and freshly charged with coal.

**191. Fining (Rabbling).**—This is an oxidizing fusion which is to volatilize Zn, Pb, As(?), Sb(?), S, to scorify Mn, Fe, Pb, Zn, Ni, Co, Bi, and some Cu, and to saturate the Cu with  $\text{Cu}_2\text{O}$ . The slags are skimmed about as fast as they are formed. At first they are black and sticky. As the impurities begin to diminish and copper is being oxidized and scorified, the slag becomes brownish and reddish, and thinner. The copper bath at the same time takes up  $\text{Cu}_2\text{O}$ . The dissolved  $\text{Cu}_2\text{O}$  gives up O to the impurities which have a stronger tendency to become oxidized than has Cu; being insoluble in Cu they rise to the surface as oxides and are taken up by the slag. Oxidation has to be stopped when slag-formation ceases and before the Cu is saturated with  $\text{Cu}_2\text{O}$ , as otherwise the latter will float on the surface as an oil-like substance. At this stage the copper holds about 6 per cent.  $\text{Cu}_2\text{O}$ . During the first of the fining the temperature is kept high, as this is more favorable to the oxidation of impurities than to that of copper; during the second part the temperature is allowed to fall a little in order to favor the formation and solution of  $\text{Cu}_2\text{O}$ .

The oxidation is hastened by "flapping," which in recent years has been replaced by the use of compressed air. Flapping consists in striking the surface of the metal from the skimming door with the edge of the head of a rabble in order to uncover the surface of the copper, and to cause waves to travel in the direction of the fire-bridge. Forcing air under a pressure of 16–20 lb. through four to six iron pipes,  $\frac{3}{4}$ –1 in. in diameter, thrust into the copper through the side doors, not only hastens the operation, but improves the product. Thus Calumet & Hecla hand-rabbed copper contained Cu, Ag 99.87, Fe 0.08, S 0.09, As 0.025 per cent. while with air-rabbling the figures were Cu, Ag 99.92, Fe 0.03, S 0.04, As 0.025 per cent.<sup>1</sup> The pipes burn off, and the oxidized iron goes into the slag. A sample of copper taken toward the end of the fining period will rise in the center of the ladle while it is solidifying on account of the  $\text{SO}_2$  set

<sup>1</sup> Private Communication, J. B. Cooper.



free by the reaction  $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} = 6\text{Cu} + \text{SO}_2$ .<sup>1</sup> The gas will break through the chilled surface and throw up liquid copper from the center in the form of small craters, similar to the sprouting of silver. The sample is said to "spew" or "throw a worm." At the same time the red-hot surface will show black specks said to be due to  $\text{Cu}_2\text{S}$  by some observers and to Fe by others.

As the fining progresses, at least with samples containing little S, the evolution of  $\text{SO}_2$  will diminish and gradually cease. In the samples taken, the rising of the surface and the specks on the latter will diminish, the fracture and color will improve, small disseminated bubbles will be found only near the surface. Fining is continued until the stage of set-copper has been reached, *i.e.*, copper holding about 6 per cent.  $\text{Cu}_2\text{O}$  in solution, when a sample will show a smooth depressed surface without any visible specks while red hot, and the fracture will reveal a single bubble beneath the apex of the depression, Fig. 10; its structure will be coarse columnar to cubical; the color brick red; there will be no luster.

The time required for fining varies from 2 to 6 hr. according to the character of the copper and the manner of assisting oxidation. As shown in Wanjukow's diagram, Fig. 411, the fining may have to be repeated with very base copper.

If the copper to be refined is rich in S, the reaction between  $\text{Cu}_2\text{S}$  and  $\text{Cu}_2\text{O}$  will be complete only if the temperature is considerably lowered. The reaction may become so violent as to project fine particles of metal from the surface in the form of a spray, or "copper rain," it is sometimes sufficiently strong to cause the metal to boil and even to foam. A true set copper can be obtained only after the decomposition of all  $\text{Cu}_2\text{S}$  is complete.

There are several studies that deal with the elimination of impurities in fining. Thus Keller<sup>2</sup> found that the relative slagability in refining converter and cathode copper was Cu 1, Pb 52.1, Sb 5.90, As 5.09, Bi 1.07, SeTe 0.84; this means that for each percentage of Cu slagged there are scorified a large amount of Pb, a smaller amount of Sb and As, and that Bi, Se, and Te are taken up by the slag in about the same proportion as in Cu. Gibb<sup>3</sup> found by com-

TABLE 94.—ANALYSES OF COPPER REFINERY SLAGS

	SiO <sub>2</sub> per cent.	FeO	Cu <sub>2</sub> O	NiO	CoO	SnO	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	PbO	Bi <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>3</sub>	SeTe	S	Ag oz. per ton	Cu
Wales <sup>4</sup> . . .	47.4	3.1	36.2	0.4	0.2	2.0	1.0	0.2	...	...	...	...	...	...	...	...	9
Kaafjord <sup>5</sup> . .	40.5	3.5	46.4	1.8	0.3	2.7	3.0	0.7	...	...	...	...	...	...	...	...	...
Baltimore <sup>6</sup> .	39.02	10.54	40.15	...	...	4.19	5.04	...	0.70	0.0020	0.2894	0.0751	0.0018	0.61	0.05	10	
Great Falls <sup>7</sup>	19.1	2.0	...	...	...	1.8	7.2	1.4	...	...	0.005	0.03	...	0.17	0.35	62.89	

<sup>1</sup> Stetefeldt, *Berg. Hüttenm. Z.*, 1863, XXII, 206.

Heyen-Bauer, *Metallurgie*, 1906, III, 83.

Doeltz, *op. cit.*, 1907, IV, 421.

<sup>2</sup> *Min. Ind.*, 1898, VII, 246; *Tr. A. I. M. E.*, 1898, XXVIII, 137, 1900, XXX, 310.

<sup>3</sup> *Tr. A. I. M. E.*, 1903, XXXIII, 653.

<sup>4</sup> Le Play, *Ann. Min.*, 1848, XIII, 503.

<sup>5</sup> Stromeyer, *Berg. Hüttenm., Z.*, 1854, XIII, 10.

<sup>6</sup> Keller, *Min. Ind.*, 1898, VII, 247.

<sup>7</sup> Burns, *Tr. A. I. M. E.*, XLVI.

parison of analyses of blister copper, refined copper, and refinery slag, that all elimination of Sb, As, and Bi was due to scorification, and none whatever to volatilization as had been supposed.

It has always been supposed that refinery slags were mixtures of various silicates. Recent investigations<sup>1</sup> seem to show that with slags running low in  $\text{SiO}_2$ , one may have to deal with ferrites,<sup>2</sup>  $\text{MO} \cdot \text{Fe}_2\text{O}_3$ , in which  $\text{MO} = \text{FeO}$  and  $\text{CuO}$ . Laboratory experiments show that these have a strong oxidizing effect. It is even suggested that roasted copper matte,  $\text{CuO}$  and  $\text{Fe}_2\text{O}_3$ , be added to a refining charge in order to hasten the removal of impurities, such as S, Pb, As, Fe, and at the same time to increase the yield in copper; nobody will again introduce Fe into a bath of Cu when he has worked hard to get rid of it.

**192. Poling.**—Poling consists in thrusting through the skimming door of the furnace into the copper the butt-end of a green pole and causing the metal to boil by means of the volatile matter set free by the heat. There may be distinguished two stages: *Dense-poling* and *Tough-poling* following one closely upon the other; in some cases they are separate operations, in others they merge into one another.

(a) **DENSE-POLING.**—The object of dense-poling is to remove by stirring, the  $\text{SO}_2$  held in solution by the melted copper as is, *e.g.*,  $\text{CO}_2$  in a glass of stale soda-water. The  $\text{C}_x\text{H}_y$ , H and CO freed from the pole, and the C have a reducing effect; hence some reduction of  $\text{Cu}_2\text{O}$  cannot be avoided in dense-poling. It may be, however, counteracted in part by keeping the side-doors of the furnace partly open. It is important that some  $\text{Cu}_2\text{O}$  remain in the copper, as the dissolving power of Cu for gas is greatly weakened by its presence.<sup>3</sup> The expulsion of gas by dense-poling is shown strikingly by the researches of Stahl<sup>4</sup> given in Table 95.

TABLE 95.—RELATION OF DISSOLVED GAS TO SPECIFIC GRAVITY OF COPPER

State of copper	Cu, per cent.	O, per cent.	Specific gravity
Dense-poled.....	.....	0.210	8.916
Tough-poled, $\frac{1}{2}$ hr.....	.....	0.123	8.851
Tough-poled, $1\frac{1}{4}$ hr.....	99.882	0.086	8.713
Dense-poled.....	.....	0.186	8.895
Tough-poled, $\frac{1}{4}$ hr.....	.....	0.164	8.887
Tough-poled, 1 hr.....	99.860	0.078	8.684
Dense-poled.....	.....	0.198	8.903
Tough-poled, $\frac{3}{4}$ hr.....	.....	0.102	8.704
Tough-poled, $1\frac{3}{4}$ hr.....	.....	0.051	8.405
Reoxidized.....	99.776	0.209	8.907

<sup>1</sup> Rauschenplat, *Metallurgie*, 1910, VII, 151.

Kohlmeyer, *ibid.*, 289.

Borchers, *ibid.*, 435.

<sup>2</sup> Hofman, "General Metallurgy," 1913, p. 466.

<sup>3</sup> Stahl, "Dissertation," Tübingen, 1886, p. 47; *Berg. Hüttenm. Z.*, 1889, XLVIII, 323; 1901, LX, 77.

<sup>4</sup> Dissertation, p. 55; *Tr. A. I. M. E.*, 1907, XXXVIII, 193; *Metallurgie*, 1907, IV, 771.

They show that a decrease in O-content is accompanied by a decrease of specific gravity, while just the reverse would have been found had it not been for the gas absorption.

Mine-plants, working their own product exclusively, carry on the entire operation of fire-refining in a single furnace. If the copper is sulphurous, dense-poling becomes necessary; if not, most of the dissolved  $\text{SO}_2$  can be expelled by allowing the set copper to cool sufficiently so that it begins to solidify at the doors; often tough-poling alone will drive out all the  $\text{SO}_2$ .

In custom-plants, treating black and blister copper of varying grades, the process from melting to fining inclusive is carried on in one set of furnaces, and the set copper then tapped into sand or cast-iron molds; the purified metal is now brought to the tough-pitch state in another set of furnaces. When the set copper is tapped and solidifies, it expels all the dissolved  $\text{SO}_2$ , and thus makes dense-poling unnecessary.

Most of the refining plants in the United States treat only high-grade (converter) copper which contains hardly any  $\text{SO}_2$ ; hence dense-poling is not carried on as an operation separate from tough-poling; further, most of the copper is charged in the solid state, and  $\text{SO}_2$  is insoluble in copper.

The practice of fining and poling simultaneously<sup>1</sup> may hasten matters, but cannot well furnish as good a product as when the two processes are kept separate.

(b) TOUGH-POLING.—The object of this operation is to reduce the  $\text{Cu}_2\text{O}$  of the brittle set copper and make the copper mechanically strong, or bring it to a "tough-pitch."

The metal bath is skimmed clean, the grate is freed from clinkers and filled with coal, the side doors are closed and luted, and poles of wood (birch, spruce), (usually two) 6–10 in. in diameter at the butt and 15–25 ft. long, thrust through the skimming door with their butt-ends in the copper, and held in an inclined position by forcing a notched plank (horse) under the protruding ends or by chaining them. The poles are pushed in as fast as they burn away. The heat of the metal chars the wood, water-vapor is set free, which stirs the copper, and  $\text{CO}$ ,  $\text{H}$ , and  $\text{C}_x\text{H}_y$ , which become more or less disseminated through it;  $\text{CO}$  and  $\text{H}$  reduce  $\text{Cu}_2\text{O}$  and are oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , both insoluble in copper; the  $\text{C}_x\text{H}_y$  are decomposed, when the  $\text{H}$  is oxidized before the  $\text{CO}$ ; the charcoal formed has its reducing effect. As the percentage of  $\text{Cu}_2\text{O}$  decreases, the oxidation of the gases diminishes, and the absorbing power of the  $\text{Cu}$  for  $\text{H}$  and  $\text{CO}$  increases; finely divided  $\text{C}$  from the dissociated  $\text{C}_x\text{H}_y$  rises unoxidized to the surface.<sup>2</sup> At some works the metal is covered with charcoal or clean egg-coke before the pole is thrust into it; at others the  $\text{C}$  is introduced only when the poling is partly finished; frequently refiners add  $\text{C}$  only toward the end of the poling in order to hold the copper at the tough-pitch stage. In all cases the charcoal or coke exerts its reducing effect upon the metal.

The progress of the reduction is followed by observing the changes in

<sup>1</sup> *Eng. Min. J.*, 1909, LXXXVIII, 735, (Peters), 988 (Laist).

<sup>2</sup> Poling with oil has been tried, but has proved successful only in part, as operation had to be finished with poles; poling with water gas is being considered.

fracture<sup>1</sup> of small ladle samples, 2 in. in diameter and  $\frac{3}{4}$  in. thick, taken at first every 10 or 15 min. and more frequently later on. A sample, chilled in water, is notched on the convex surface with a chisel, placed in a vise, and given a shearing blow with a hammer. If a small ingot,  $12 \times 2 \times 2$  in., is cast as test-piece, this is nicked to a depth of  $\frac{1}{8}$  in., supported at the ends and then broken by the pressure of a screw or the piston-rod of a steam cylinder.<sup>2</sup> The structure of the fracture is at first columnar and coarse; it may pass through cubical and coarse, radiated and coarse, finely radiated, somewhat granular, granular and finely radiated, to reach finely granular and finely radiated (fibrous). The color at first a dark brick red, becomes a lighter brick red, shades off into rose color, and finally becomes a true rose color. The luster, at first absent, appears in the form of specks of silkiness, which increase in size, until the entire surface has a silky appearance.

Additional tests<sup>3</sup> are those for malleability, electric conductivity, torsion, microstructure and for brass-making.

**MALLEABILITY.**—(a) A hemispherical sample is placed in a vise with plane surface uppermost and bent.

(b) A small ingot is forged or drawn into a rectangular bar, and then twisted into the form of spiral.

(c) A button, 2 in. in diameter and 2 in. thick, with handle, is cast and the button hammered to a thin disc.

(d) A flat sample ingot is hammered out and bent to and fro.

(e) Another ingot, just after it has solidified but is still red hot, is bent upon itself.

In none of these tests may there appear any cracks.

**ELECTRIC CONDUCTIVITY.**<sup>4</sup>—A test bar 1 in. square and 8 in. long is heated and rolled into a  $\frac{1}{4}$ -in. rod, annealed, drawn cold through Nos. 2, 4, 6, 8, 10 to a No. 12 wire B. & S. gauge, finished through a diamond die to 0.0808 in. diameter, and tested in a Willyoung or a Hoopes conductivity bridge.

**TORSION.**—Tests are made with the same wire: two clamps set 6 in. apart hold the wire, one of them is rotated until the wire breaks; 40 twists with 1 per cent. elongation is a required figure for wire-bars.

**MICROSTRUCTURE.**—The microscopical examination of the polished surface of a sample furnishes a rapid method for determining the amount of  $\text{Cu}_2\text{O}$  present (page 14).

**THE BRASS TEST.**—This test formerly very common has fallen into disuse: 60 pt. copper are melted in a crucible under a charcoal cover, 40 pt. zinc are stirred in with an iron rod; the brass formed is cast into a small ingot,  $1\frac{1}{4}$  in. square and 4 in. long, and allowed to cool slowly. With impure copper, the fracture is columnar to coarsely fibrous, two diagonal lines are clearly visible, the color is dark yellow, and there is no luster; with pure copper, the fracture is

<sup>1</sup> Hofman-Green-Yerxa, *Tr. A. I. M. E.*, 1904, XXXIV, 694.

<sup>2</sup> Heath, *Proc. Lake Sup. Min. Inst.*, 1901, VII, 73.

<sup>3</sup> Heath, *op. cit.*, *Min. Inst.*, 1901, VII, 68.

<sup>4</sup> Burns, *Tr. A. I. M. E.*, 1913, XLVI.

finely granular, there are no diagonal lines, the color is light yellow, and the luster silky. Chemical analysis<sup>1</sup> shows what impurities are present.

Tough-pitch copper is always allowed to retain some  $\text{Cu}_2\text{O}$ , as it insures the presence of all impurities as oxides as long as these have a greater affinity for O than has Cu, and as it is a controlling factor of the amount of gas held in solid solution by the copper, which in its turn governs the greater or smaller crowning of the surface of an ingot, bar, or cake. An average figure is perhaps 0.7 per cent.  $\text{Cu}_2\text{O}$ ; with a heavy cake it will be higher, as this holds more gas than a wire-bar, for which the  $\text{Cu}_2\text{O}$  will be kept lower. The rôle that a small admixture of Fe or S may play is not definitely settled.

C. OVERPOLING.—If the reduction in poling is carried too far, the copper gives off gas (spews, throws a worm), becomes porous and brittle, yellowish, and assumes a brilliant luster; it has been overpoled,<sup>2</sup> too much  $\text{Cu}_2\text{O}$  has been reduced to Cu, and foreign substances have been changed from the oxide to the metallic state. If the copper has been only slightly overpoled, *i.e.*, when the casting begins to show excessive crowning, rabbling the copper, to cause some  $\text{Cu}_2\text{O}$  to form, will correct the evil. If the overpoling is decided, the charge has to be worked over, *i.e.*, the charcoal removed, the copper reoxidized to set copper and poled again. Correcting the great lack of  $\text{Cu}_2\text{O}$  by rabbling alone does not mend matters satisfactorily, as it becomes next to impossible to hold the copper at the proper pitch while casting. An explanation of this fact is still lacking.

Certain metals and alloys have been used for the toughening of copper. Thus  $\text{Pb}$ <sup>3</sup> is to assist in expelling gas, in scorifying  $\text{Cu}_2\text{O}$  or reducing it and thus make the copper more malleable;  $\text{Cu}_3\text{P}$ ,<sup>4</sup>  $\text{Cu}_7\text{Mn}$ ,<sup>5</sup>  $\text{Si}$ ,<sup>6</sup>  $\text{Mn}_2\text{Si}$ ,<sup>7</sup>  $\text{Fe}_x\text{Si}$  for arsenical copper,<sup>8</sup>  $\text{Mg}$  or  $\text{Cu}_x\text{Mg}$ ,<sup>9</sup>  $\text{BO}$ <sup>10</sup> have been and in some cases are used for the reduction of  $\text{Cu}_2\text{O}$  and for preventing the oxidation of copper while casting.

<sup>1</sup> Heath, *J. Am. Chem. Soc.*, 1905, XXVII, 308, 1907, XXIX, 607.

<sup>2</sup> Hofman-Hayden-Hallowell, *Tr. A. I. M. E.*, 1907, XXXVIII, 171.

<sup>3</sup> Egleston, *Tr. A. I. M. E.*, 1881, IX, 705.

Stahl, *Berg. Hüttenm. Z.*, 1890, XLIX, 127.

Keller, *Min. Ind.*, 1898, VII, 233.

Jolibois-Thomas, *Rev. Mét.*, 1913, X, 1264.

<sup>4</sup> Hampe, *Zt. Berg. Hütten. Salin. Wesen i. P.*, 1876, XXIV, 8; *Berg. Hüttenm. Z.*, 1876, LV, 158.

Rössler, *op. cit.*, 1878, XXXVII, 370; 1879, XXXVIII, 139; *Zt. Berg. Hütten. Salin. Wesen i. P.*, 1879, XXVII, 14.

<sup>5</sup> Parsons, *Eng. Min. J.*, 1876, XXXI, 366.

Rössler, *Berg. Hüttenm. Z.*, 1878, XXXVII, 370.

<sup>6</sup> *Brass World*, 1905, I, 199.

<sup>7</sup> Gloger, *Metallurgie*, 1906, III, 253.

<sup>8</sup> Johnson, *J. Inst. Met.*, 1913, X, 275; *Eng. Min. J.*, 1913, XCVI, 648, 833.

<sup>9</sup> *Oest. Zt. Berg. Hüttenw.*, 1901, XLIX, 546; *Eng. Min. J.*, 1902, LXXIV, 372.

Sperry, *Brass World*, 1905, I, 43.

Hüsen, *Metall-Erz.*, 1912, X, 480, 490; 1913, XI, 518.

Jolibois-Thomas, *Rev. Mét.*, 1913, X, 1264.

<sup>10</sup> Weintraub, *Tr. Am. Electrochem. Soc.*, 1910, XVIII, 207; *Met. Chem. Eng.*, 1910, VIII, 629; 1912, X, 433, 536; *Brass World*, 1912, VIII, 355; *Metal Ind.*, 1912, X, 462; *Tr. Am. Inst. Met.*, 1912, VI, 138.

Thomson, *Met. Ind.*, 1913, XI, 8; *Tr. Am. Inst. Met.*, 1913, V, 101.

TABLE 93.—COPPER REFINING FURNACES

	Belbach S. & R. Co.	U. S. Metals Refining Co.	Boston & Montana Copper Mg. Co.	Anaconda Copper Mg. Co.	Eastern Anode Furnace	Raritan Copper Works	Nichols Copper Co.	Mansfield, Eckhard Works	Mansfield, Eckhard Works	Mansfield, Kupferham- mer Works
Length of hearth, ft. in. ....	23' 3"	34' 7½"	23' 6½"	27' 9"	31' 0"	33' 8"	32' 0"	14' 9½"	19' 5½"	16' 4½"
Width of hearth at bridge, ft. in. ....	6' 9"	14' 10"	7' 1½"	14' 8"	8' 0"	17' 0"	16' 6"	6' 6½"	6' 6½"	5' 10½"
Width of hearth at middle, ft. in. ....	13' 10"	14' 10"	14' 8"	14' 8"	15' 7"	17' 0"	16' 6"	9' 10½"	9' 10½"	9' 2½"
Width of hearth at flue, ft. in. ....	1' 6"	1' 6"	1' 8"	1' 10"	1' 6"	2' 0"	6' 2"	2' 1½"	2' 1½"	2' 1½"
Hearth area, sq. ft. ....	274	401	259	322	400	492	500	75.3	107.6	102.4
Hearth depth, in. ....	20"	30"	12-13"	23.5"	31.5"	22"	31"	51"	51"	51"
Hearth thickness, in. ....	16 and 18"	30"	30"	31"	31"	30"	20"	27½"	27½"	27½"
Hearth material . . . . .	Sand	Sand and roll- ing-mill scale	Sand, 94 per cent. SiO <sub>2</sub>	Silica brick top course 20", bot- tom 12"	Silica gravel	21" sand 9" brick	Sand and fire-brick	Sand	Sand	Sand
Hearth support. ....	Cast-iron plates	Cast-iron plates	Solid and central flue	Solid	Cast-iron plates	Cast-iron plates	Concrete, 6" thick	Brick arch and silice- ous sand- stone	Brick arch and silice- ous sand- stone	Brick arch and siliceous sandstone
Grate, length, ft. in. ....	7' 0"	9' 0"	8' 6"	7' 0"	6' 11.5"	8' 0"	8' 0"	2' 5½"	3' 5½"	2' 3½"
Grate width, ft. in. ....	6' 0"	8' 0"	7' 1½"	5' 6"	8' 0"	10' 0"	11' 0"	4' 1½"	4' 1½"	4' 1½"
Grate, depth, below top of bridge at bridge, ft. in. ....	4' 8"	4' 9"	2' 6"	2' 7"	4' 8"	5' 7½"	3' 0"	2' 5½"	2' 5½"	1' 10½"
Grate, depth below top of bridge at opposite end, ft. in. ....	4' 8"	4' 9"	2' 6"	2' 7"	4' 8"	5' 7½"	3' 0"	2' 5½"	2' 5½"	1' 7½"
Grate, area, sq. ft. ....	42	72	61	38.5	56	80	88	10.1	14.1	9.4
Ratio, hearth to grate area. ....	6.4:1	6.4:1	4.2:1	8.36:1	7.1:1	6.1:1	5.7:1	7:1	8:1	10.8:1
Roof, height above bridge, ft. in. ....	2' 0"	3' 6"	2' 3"	2' 0"	2' 2.5"	3' 3"	3' 5"	1' 6½"	1' 6½"	1' 7½"
Roof, height above hearth at bridge, ft. in. ....	5' 1"	4' 9"	3' 8"	6' 2.5"	5' 1"	4' 6"	6' 0"	2' 9½"	2' 9½"	2' 11½"
Roof, height above hearth at flue, ft. in. ....	3' 8"	2' 11½"	1' 5"	3' 8"	3' 4"	4' 1"	3' 0"	1' 2½"	1' 2½"	1' 6½"
Bridge, width, ft. in. ....	3' 6"	4' 1"	3' 0"	3' 9.5"	3' 6"	4' 4"	4' 10"	4' 1½"	4' 1½"	4' 1½"
Vulcuary (flue leading out of roof), ft. in. ....	3' 9"	2' 6" X 5' 6"	3' 9" X 1' 7"	1' 6"	2' 0"	10.5 sq. ft.	6' X 4'	4' 1½"	4' 1½"	4' 1½"
	X 1' 10½"			X 4' 6"	X 4' 8"			1' 8½" X ?	1' 8½" X ?	1' 8½" X ?
Flue leading to chimney, to boiler, ft. in. ....	3' 9"	2' 6" X 5' 6"	2' 0" X 1' 7"	2' 2' 1"	2' 0"	16.5 sq. ft.	6' diam.	1' 9½"	1' 9½"	.....
Chimney, inside diameter, ft. in. ....	3' 4½" sq.	5' induced draft	2' 8" sq.	X 2' 4"	X 6' 0"	96' at 71" diam. 30' at 62" diam.	10'	X 1' 6½"	X 1' 6½"	413"
				3' 3"	X 3' 9"			2' 4"	2' 4"	
								X 2' 4"	X 2' 4"	
Chimney, height, ft. ....	77' above grate	79' induced draft	80'	74'	95'	126	200'	44'	44'	132'
Waste-heat boiler, number, kind, h.p.	One 200 h.p. Wickes	One 515 h.p. Worthington	None	None	One 335 h.p. Stirling!	None	One water- tube, 780 h.p.	None	None	None

1 Waste-heat boiler stack, diameter 5', height above ground line 146'.

TABLE 93.—COPPER REFINING FURNACES—(Continued)

	Balbach S. & K. Co.	U. S. Metals Refining Co.	Boston & Montana Copper Mg. Co.	Anaconda Copper Mg. Co.	Eastern Anode Furnace	Raritan Copper Works	Nichols Copper Co.	Mansfield, Eckhard Works	Mansfield, Eckhard Works	Mansfield, Kupferham- mer Works
Charge, character.....	Cathode copper	Cathode copper	Cathode copper	Liquid con- verter cop- per ladle- skulls	Blister copper	Cathode copper	Cathode copper	Residue from Zier- vogel proc- ess and coal	Impure copper 34 and 44 per cent. Cu	Copper drosses, odds and ends
Charge, time of working, total hr.....	24	24	24	16	26	24	24	24	24	20-30 90-120 1
Charge, time of charging, total hr.....	2-2.5	1.25	2	Scrap 1-2 liquid cop- per 8	.....	2.5	16	1	1- $\frac{1}{2}$	.....
Charge, time of melting and raking, hr.....	12-14	.....	16	.....	14	8.75	16	12-14	10	7-8 12-18 11-22 78-108
Charge, time of fining, hr.....	2	16	1 $\frac{1}{2}$	15 lb. air when fur- nace $\frac{1}{2}$ full	.....	5.5	2-3	4-5	5-6	.....
Charge, time of poling, hr.....	2	.....	2 $\frac{1}{2}$	.....	3	2.5	2-3	1-1 $\frac{1}{2}$ dense 1 tough	1 $\frac{1}{2}$ dense 1 $\frac{1}{2}$ tough	.....
Charge, time of ladling, hr.....	.....	.....	3-4 wire-bar has the ingot	.....	.....	.....	.....	2 $\frac{1}{2}$	3	Tapped
Charge, time of casting, hr.....	3.5-4	See p. 401	.....	4-5 depend- ing on size of anodes	5	4.75	5	.....	.....	.....
Charge, time of cleaning up, etc.....	0.5	.....	2	.....	4	.....	.....	.....	.....	2
Charge, tons in 24 hr.....	80	200-250	40	150	134 charge 145	200-250	250	12-14 tons residue, 8- 9 per cent. coal	$\frac{1}{2}$ -1 11	6+(1-2)
Charge, tons per sq. ft. of hearth in 24 hr.....	0.332	0.466	0.154	0.466	0.335	0.5±	0.5	0.120	0.083	0.083
Charge, tons per ton coal.....	12.5	8.33	3.3	13.96	8.15	7.00	10.00	4.0	4.2	3.3
Coal, ash per cent.....	6-7	7	20.3	12.17	13.75	7.1	8.50	10-12	10-12	1.1
Coal, fixed carbon per cent.....	60-70	73	50.9	45.42	70.75	74.0	70-76	.....	.....	.....
Poles, kinds, no. per charge.....	Hard wood 8-12	.....	Green pine, 40(25' l. 4 $\frac{1}{2}$ " -5' butt)	Soft pine 40-50 (18 -25' l. 4 $\frac{1}{2}$ " diam.)	18	Hard wood 25 (35' l. 3" butt	Hard wood 14-16	Beach, oak, birch, 12-13	Beach, oak, birch, 10-11	.....
Charcoal, kind, lb. per charge.....	400	Coke	455	Unused ends of poles	1273	12 lb. char- coal and coke per ton copper	2000	Hard, 330	Hard, 330	.....

TABLE 93.—COPPER REFINING FURNACES—(Continued)

	Balbach S. & R. Co.	U. S. Metals Refining Co.	Boston & Montana Copper Mfg. Co.	Anaconda Copper Mfg. Co.	Eastern Anode Furnace	Raritan Copper Works	Nichols Copper Co.	Mansfield Beckhard Works	Mansfield Beckhard Works	Mansfield Kupferham- mer Works
Labor, in 8-hr. shift.....	7-8 day 2 night	13 for 24 hr.	4 furnace and dipping crew	8	.....	12 days 2 nights	.....	6 A. M. 2½ rest of time	6 A. M. 2 rest of time	2
Copper produced, character.....	Anode wire-bar	Wire-bar ingot	Wire-bar, 38% Cake, 37% Ingot, 19% Plate, 1% Billets, 5%	Anodes	Anodes	Wire-bar	Wire-bar, slate, ingot- bar, cake	Cake and ingot	Cake	Impure
Copper, per cent. of charge.....	98-99	97	97-22	98	99-7	99-6	99-95-99-97	62-63	93	84
Copper, manner of casting.....	Walker machine	Improved Walker machine	Ladle hung from trolley	Endless chain (Mc- Coy machine)	Machine	Clark machine	Nichols casting machine	Hand	Hand	44 Tap
Slag, SiO <sub>2</sub> .....	50	44 insol.	19-7	19-1	39	25	32	17-25	.....	.....
Fe(MnO)O.....	2-5	4	2-4	25-5	3-1	.....	.....	7-10	.....	.....
Al <sub>2</sub> O <sub>3</sub> .....	Variable	Variable	2-3	1-9	.....	.....	.....	4-5-6	.....	.....
CaO.....	Variable	1	15-0	2-1	.....	.....	.....	1	.....	.....
Cu.....	35-50	45	55-2	40-1	38	55	45	42-46	.....	.....
Slag per cent. of charge.....	2-5-3-0	3	4-4	4	2-2	0-22-1-00	0-5	22-5	.....	23-2 68-7
Slag disposition.....	Blast- furnace	Blast furnace or converter	Converter	Converter	Blast- furnace	Blast- furnace	Blast- furnace, matte converter	Blast- furnace	Blast- furnace	Stamp mill, screw, over- size back to furnace, undersize (rich in Ni) sold



**193. Examples of Refining.**—Three graphic representations of the changes taking place in refining will furnish details of the chemical and physical changes outlined in the preceding discussion.

Wanjukow<sup>1</sup> studied by means of chemical analyses the changes that took place in refining a charge of 4450 lb. of impure black copper Cu 94.55, Ag 0.0021, Pb 0.0123, Fe 3.0373, Co 0.8944, Ni 0.4080, P 0.0105, As 0.1257, Sb 0.0020,

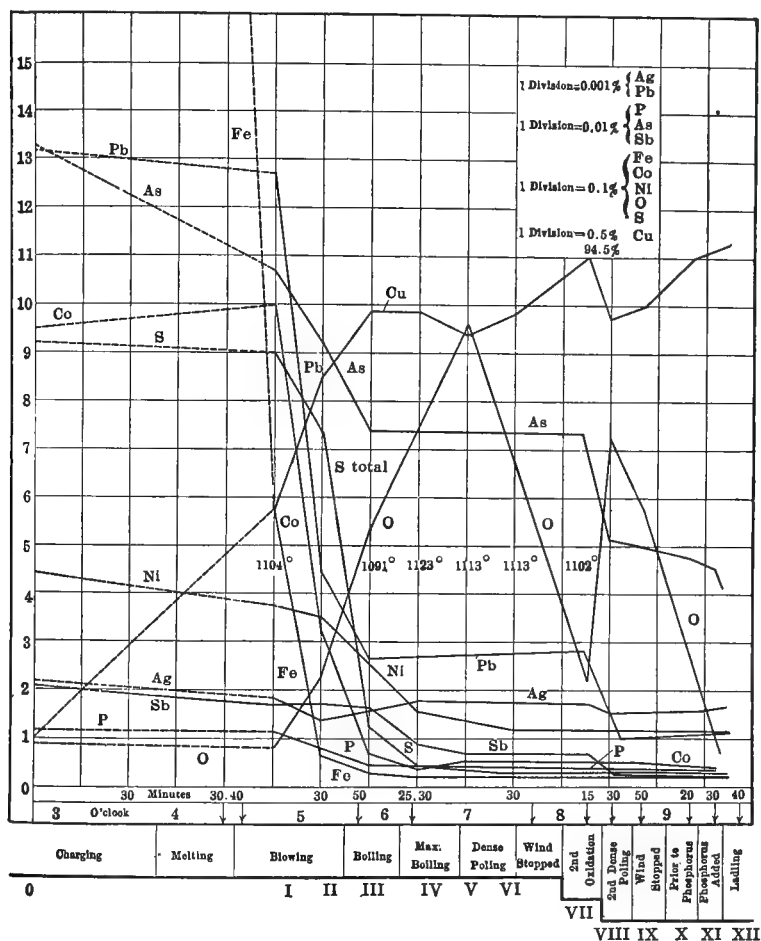


FIG. 411.—Elimination of impurities in refining black copper (Wanjukow).

O 0.0953, S 0.8678, SO<sub>2</sub> 0.0006, Insol. 0.0004; total 100.0064 per cent. in a reverberatory furnace provided with two tuyères and heated with producer gas generated from twigs, brush-wood and pine-needles. The copper was brought to tough-pitch by two consecutive refinings. The results are drawn in Fig. 411. The abscissa gives the time and the different stages of the process. Thus, gas and air are turned on at 2.22 o'clock, charging is begun at 2.23 and finished at

<sup>1</sup> *Metallurgie*, 1909, VI, 749, 792.

3.30. At 4.30 the charge is melted; at 4.40 the blast is turned on; boiling begins at 5.50 and reaches its maximum at 6.25-6.30. At 7.00 boiling ceases and poling is begun, which is a dense-poling. At 7.38, the blast and other access of air are shut off, whereby dense-poling changes into tough-poling. At 8.15 the copper is at tough-pitch. The second oxidation is started by turning on the blast; at 8.30 the second dense-poling begins, lasts until 8.50, when the blast is shut off and thereby again dense-poling changed into tough-poling. This continues until 9.30, when P is added. At 9.40 ladling the refined copper is started.

The ordinate represents percentages on the basis of 100 parts of Cu (which changes the analysis above to Cu 100, Ag 0.0022, Pb 0.0130, Fe 3.2124, Co 0.9455, Ni 0.4312, P 0.0111, As 0.1328, Sb 0.0215, O 0.1009, S 0.9173) and gives the relative eliminations of impurities. A different scale is employed for certain impurities as explained in the legend in Fig. 411. The lines covering the period of charging to complete fusion, 2.23 to 5.00 o'clock, are dotted, as their positions have not been determined; they indicate the probable rates of oxidation.

The refined copper gave upon analysis the figures shown in Table 96.

TABLE 96.—ANALYSIS OF REFINED COPPER

Cu	Ag	Pb	Fe	Co	Ni	P	As	Sb	O	Sso <sub>2</sub>	S total	Total
99.66	0.0016	0.0010	0.0080	0.0243	0.1091	0.0012	0.0402	0.0017	0.00486	tr.	0.1093	99.9051
100.00	0.0016	0.0010	0.0080	0.0244	0.1095	0.0012	0.0403	0.0017	0.00487	.....	0.1093	.....

The curves show the following:

*Fe* is oxidized during the melting-period and quickly scorified as soon as the copper has become liquefied, falling to 0.0080 per 100 parts Cu at the beginning of the boiling period; from then on the elimination progresses more slowly.

*Co*.—The rise in the Co-curve during the melting period would indicate that Co was not oxidized; the contrary is true, but CoO is unstable at a red heat. The rapid drop of the curve after fusion shows that Co is scorified nearly as fast as is Fe; at the beginning of the boiling, the elimination is weaker; at the strongest boiling, it reaches 0.024 per 100 Cu and then practically ceases.

*Ni*.—This metal is difficult to slag; the refined metal retains as much as 0.11 per 100 Cu. At first, oxidation and scorification progress very slowly; after most of the Fe and Co have been slagged (before the boiling-stage) the elimination progresses more rapidly, then slows up when boiling is in full progress, and finally ceases. The first refining operation has taken out all the Ni that can be removed, so repeating the process does little good.

*S*.—Some S is oxidized in melting the charge; the elimination then proceeds more quickly but still very slowly until most of the Fe has been scorified, when with the lowering of the temperature from 1109 to 1091° C. the boiling period sets in, and SO<sub>2</sub> is set free rapidly bubbling up through the copper (copper rain), and the S-content drops from 0.7189 to 0.0911 per 100 Cu; from now on the evolution of gas goes on more slowly reaching 0.0379 in stage IV, 0.0256 in stage V (dense-poling), and 0.0097 in stage VI, when the S-content changes little.

**O.**—The metal takes up O during the melting; the O-content rises quickly during the fining period and especially so after the Fe and part of the Co and Ni have been scorified; boiling assists the formation of  $\text{Cu}_2\text{O}$ . With the beginning of the poling, the percentage of O falls quickly and regularly; it increases with the second oxidation and decreases again with the second poling.

**Pb.**—This metal is scorified during both oxidizing periods, more quickly in the first, when there is more Pb present, than in the second; little Pb is driven off after this.

**Ag.**—A small amount of Ag enters the slag with the Pb.

**Sb.**—This metal, difficult to eliminate, appears to be slagged to a greater extent during the melting than the fining period; the boiling of the copper is favorable to oxidation.

**As.**—The behavior of As is similar to that of Sb; a large part is oxidized in melting, fining favors elimination, poling has no effect.

The second refining stage appears favorable to the scorification of both Sb and As.

The second example of refining impure copper is that of Stahl<sup>1</sup> who treated at Mansfeld, Germany, in the usual course of work two 10-ton charges of blister copper in about 21 hr. at temperatures ranging from 1200 to 1450° C., and took samples for chemical analysis at the end of each stage of the process. The results of one of his tests are given in Table 97 and plotted in Fig. 412.

TABLE 97.—STAHL, ELIMINATION OF IMPURITIES IN REFINING BLISTER COPPER

	Blister copper		After melting		After fining		After dense-poling		After tough-poling	
	Per cent.	Per 100 Cu	Per cent.	Per 100 Cu	Per cent.	Per 100 Cu	Per cent.	Per 100 Cu	Per cent.	Per 100 Cu
Cu....	98.140	100.000	98.950	100.000	98.550	100.000	99.060	100.000	99.300	100.000
Ag....	0.011	0.011	0.010	0.010	0.010	0.010	0.009	0.009	0.009	0.009
Pb....	1.060	1.080	0.330	0.330	0.160	0.160	0.190	0.190	0.170	0.017
Ni....	0.610	0.620	0.350	0.350	0.350	0.350	0.360	0.360	0.360	0.360
As....	0.058	0.059	0.058	0.059	0.055	0.056	0.057	0.057	0.054	0.054
O.....	0.121	0.123	0.302	0.306	0.875	0.888	0.324	0.329	0.107	0.108
Total..	100.000	.....	100.000	.....	100.000	.....	100.000	.....	100.000	.....

In refining impure Cu the elimination of impurities does not proceed in a fixed order or at a given rate, but is governed rather by the amount of impurity and the form in which it is present, by the lining of the reverberatory furnace (acid or basic), the size of the charge, the admission of air, the temperature and other details of the mode of operating. The work of Wanjukow and Stahl shows, whatever may be the variations as to detail, in general: (1) that Zn, Fe, Co, Sn are removed completely at the beginning of the fining period, and S at end of dense-poling; (2) that the elimination of Ni, Pb, As, and Sb continues through the entire process and is imperfect; and, (3) that Ag and Bi are re-

<sup>1</sup> *Metallurgie*, 1912, IX, 362, 377.

moved only to a very small extent, the former mainly by volatilization, the latter by scorification.

Hofman-Hayden-Hallowell<sup>1</sup> followed the chemical and physical changes that took place in cathode copper as it passed through a 100-ton refining furnace to be cast into wire-bar. The results are given in Fig. 413.

Sample No. 1 was taken after melting and skimming, No. 2 after fining for 6 hr. with compressed air when the stage of set copper was reached; samples Nos. 3 to 11 at 15-min. intervals during tough-poling; No. 11 represents tough-pitch copper; Nos. 12 and 13 overpoled copper.

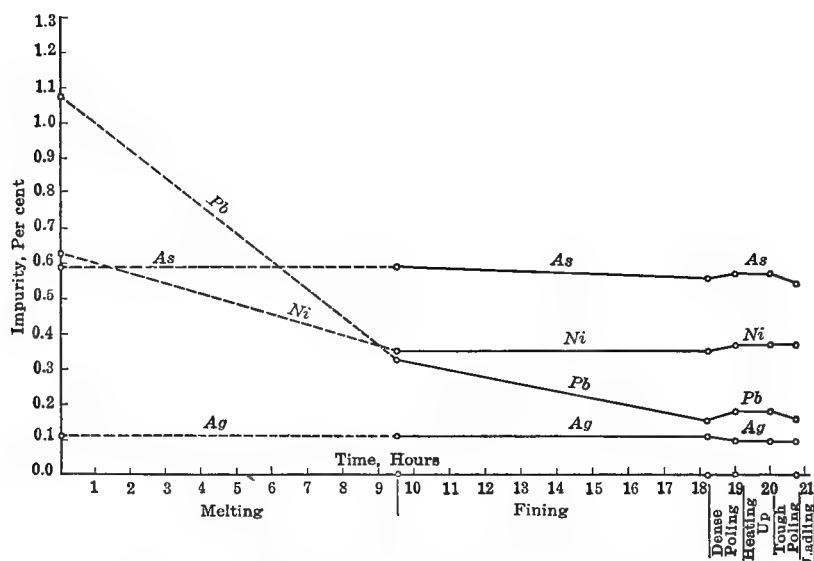


FIG. 412.—Elimination of impurities from blister copper (Stahl).

On the whole, the chemical changes up to the tough-pitch stage are what would be expected; the physical properties are in harmony with the rise and fall of the Cu-content. The percentage of FeO, usually lower than that of S, is higher; it was reduced to 0.086 per cent. by 6 hr. fining and reached the minimum of 0.022 per cent. only after poling for 15 min., the probable reason being that some Fe was taken up from the iron pipe conveying compressed air into the copper, and removed only after the pipe had been withdrawn. Practically no S was driven off; the 0.030 per cent. S, high for electrolytic copper, remained about constant. The specific-gravity and electric-conductivity curves show the same general trend as does that of the Cu-content. The tensile strength shows a gradual decrease as the poling progresses, and the elongation a corresponding increase. Before taking samples Nos. 12 and 13, the bulk of the copper in the furnace was cast, and the remaining small amount overpoled until it threw a worm. No regularity can be expected from these two samples.

<sup>1</sup> *Tr. A. I. M. E.*, 1907, XXXVIII, 171.

Clevenger<sup>1</sup> gives the following temperatures as averages of a number of refining furnaces: Charge melted and ready to rabble  $1141^{\circ}\text{C}.$ ; after 25 min. rabbling

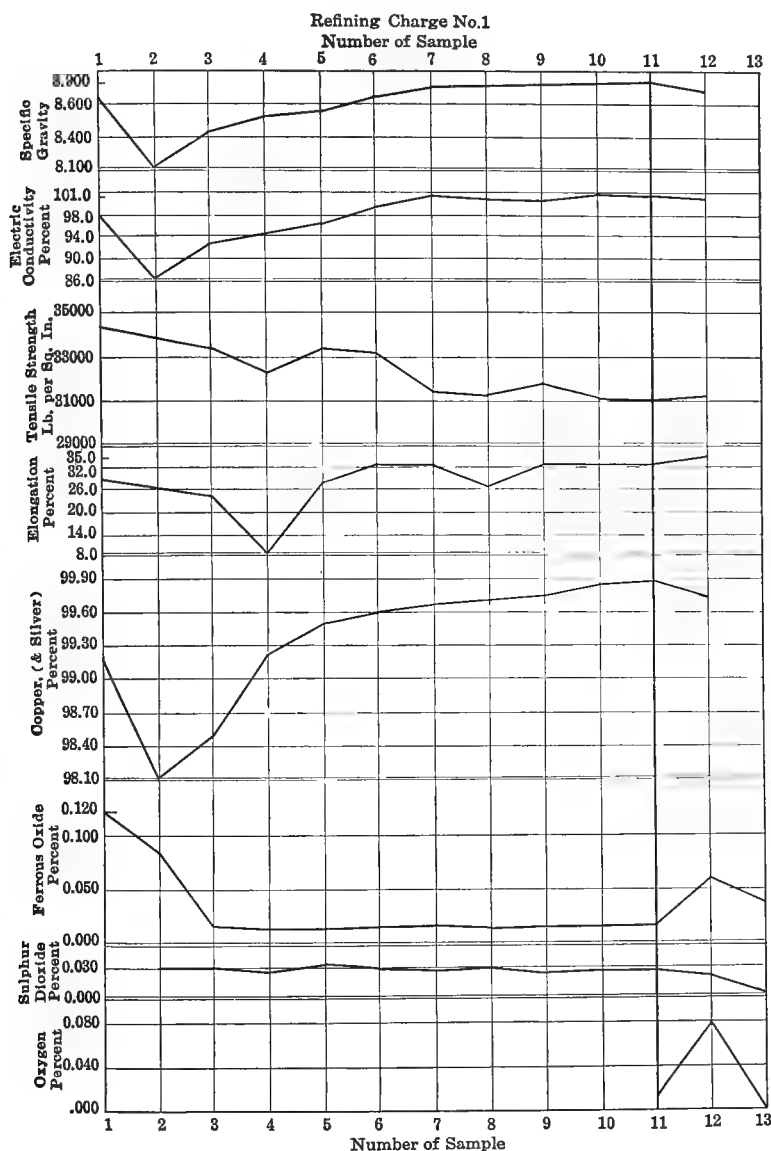


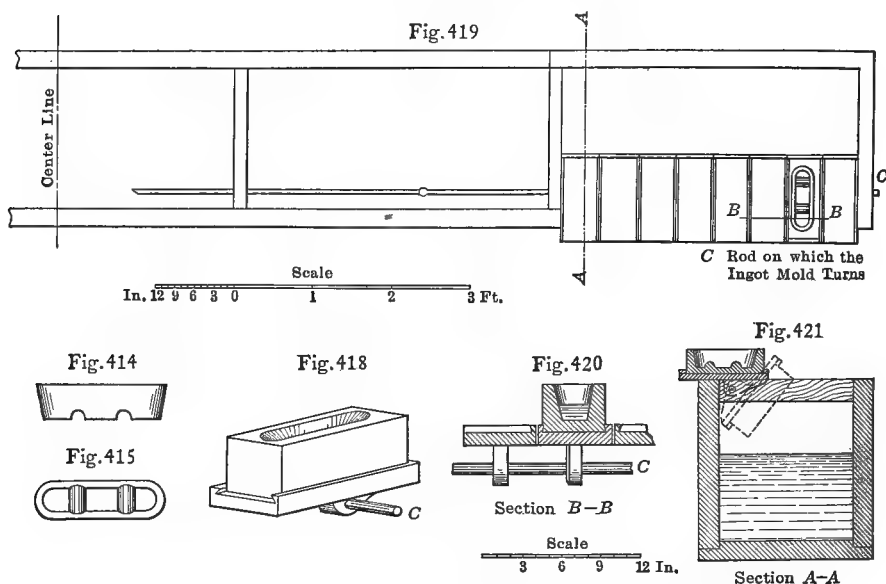
FIG. 413.—Changes in refining cathode copper.

$1103^{\circ}$ ; after 75 min.  $1103^{\circ}$ ; at end of rabbling  $1103^{\circ}$ ; after 20 min. poling  $1107^{\circ}$ ; before ladling  $1125^{\circ}$ , after ladling 20 min.  $1121^{\circ}\text{C}.$

**194. Casting.**—When the copper has “come to nature” or arrived at the tough-

<sup>1</sup> *Mel. Chem. Eng.*, 1913, XI, 448.

pitch stage, it is ready to be cast into marketable forms. These are ingots, ingot-bars, wire-bars and cakes. The ordinary three-heel ingot is shown in Fig. 414-415; it is usually  $3 \times 3 \times 9$  in. and weighs about 17 lb. The weight ranges from 10 to 22 lb., e.g., Raritan 10-16 lb.; Phelps-Dodge & Co. and American Smelting & Refining Co. 18-20; Calumet & Hecla 20 lb.; ingots in a shipment vary 2 and 3 lb. in weight. For convenience in shipping the copper is cast sometimes in the form of ingot-bar, Fig. 416,  $3 \times 3 \times 27$  in., which is readily broken at the two deep webs into ingots of ordinary size. Beside the three-heel form, there are molded one-heel, four-heel ingots, etc.<sup>1</sup>



FIGS. 414-415. FIGS. 418-421.—Casting copper-ingots by hand.

THE INGOT MOLD is of cast copper. Fig. 417 shows the press in which it is formed. The platform, *d*, carries the diagonally-split cast-iron mold, *f*, and the iron frame, *a*, with lever, *e*, to which is attached rod, *b*, carrying the iron disc, *c*. The iron mold is filled two-thirds with copper, the disc is pressed down until the metal rises to the surface, is held there until the metal comes to a set, and then raised. The clamps holding the split mold together are loosened, the ingot-mold is turned out, and another cast.

Ingot-molds are slipped into reversible cast-iron shoes, Fig. 418, through which passes the rod, *c*. A number of such molds, eight in Figs. 419-421, are placed in a row over a water-trough with continuous inlets and outlets for cooling water. The trough (bosh) is made either of wood and the bottom lined with sheet iron, or of cast iron; it is placed from 10 to 15 ft. from the ladling door of the furnace. As soon as a cast ingot has come to a set, the mold is

<sup>1</sup> *Metal Ind.*, 1903, I, 93; *Brass World*, 1905, I, 81.

tilted, Fig. 421, and the ingot dumped into the water to hinder oxidation. Here it cools, and is removed with tongs from the opposite side; the top is brownish from oxidation, the sides and bottom are only tarnished.

THE LADLES used for casting are about 9 in. in diameter, 5 in. deep, and hold from 30 to 45 lb. copper; they are of wrought iron and have D-handles. Before using, the bowl receives a clay wash, is dried, brought to a red heat in the fur-

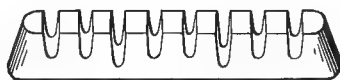


FIG. 416.—Ingot-bar.

nace, and is then swashed in the copper to prevent skulls from forming later on. From four to six, and perhaps more, men will ladle the copper from the furnace. Given 24 hr. as the time to finish a charge, the maximum furnace capacity is 20 tons which can be hand-ladled in about 5 hr.

WIRE-BARS, Figs. 422-424, are trapezoidal bars 33-60 in. long,  $3\frac{1}{4}$ - $4\frac{1}{8}$  in. wide at the top,  $2\frac{7}{8}$ - $3\frac{5}{8}$  in. at the bottom, and  $3\frac{1}{4}$ - $4\frac{1}{8}$  in. thick; the ends are usually

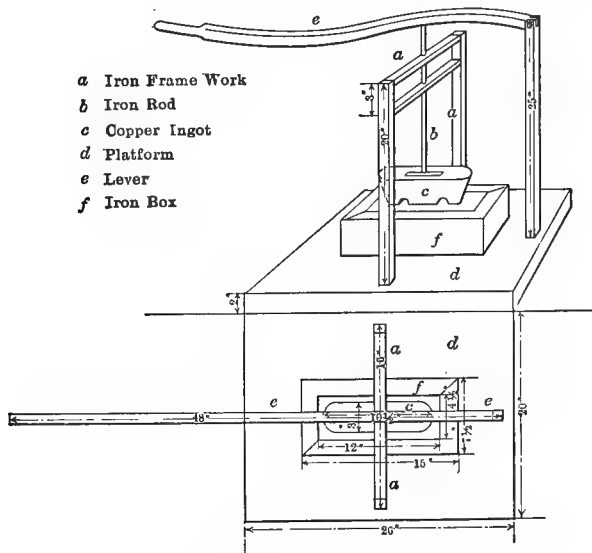
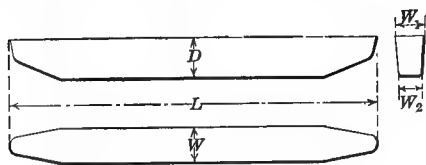


FIG. 417.—Ingot-mold press.

tapered; the weight ranges from 85 to 250 lb. The molds are of copper, and are cast in the same manner as are ingot-molds; however, the die is water-cooled to counteract the expansion of the iron, which might crack the copper. The molds standing on the floor are smoked or washed with a bone-ash emulsion before every cast to furnish smooth bottom and sides; the bars are dumped singly into water as are ingots. Water with 1 per cent.  $H_2SO_4$  gives them a good

color. In order to insure complete filling of a wire-bar mold without any chilling of the surface, it is important that the stream of copper be continuous. This is accomplished by the use of large (bull) ladles.<sup>1</sup> These are long-handle ladles holding 100 lb. copper or more, suspended by a chain or rod from an overhead trolley which is sometimes circular. The full weight of the bar can then be dipped from the furnace and poured into the mold without any interruption.



FIGS. 422-424.—Wire-bar.

CAKES are square or round flat castings; square cakes range from 14×17 in. to 42×42 in., round from 8 to 39 $\frac{3}{8}$  in.; the thickness of either class varies from 1 $\frac{1}{2}$  to 8 in. Large cakes

are cast in open iron split molds placed on a copper or iron base. A cast cake is allowed to cool in the mold; when cold, a second cake is often cast on top of the first; the oxidized surface of the lower prevents adhesion of the bottom of the upper cake.

THE CASTING TEMPERATURE of copper ought to be low, as a high temperature causes rising in the mold. A casting should have a level, in some cases a slightly crowned surface which appears ruffled and is brownish from oxidation.

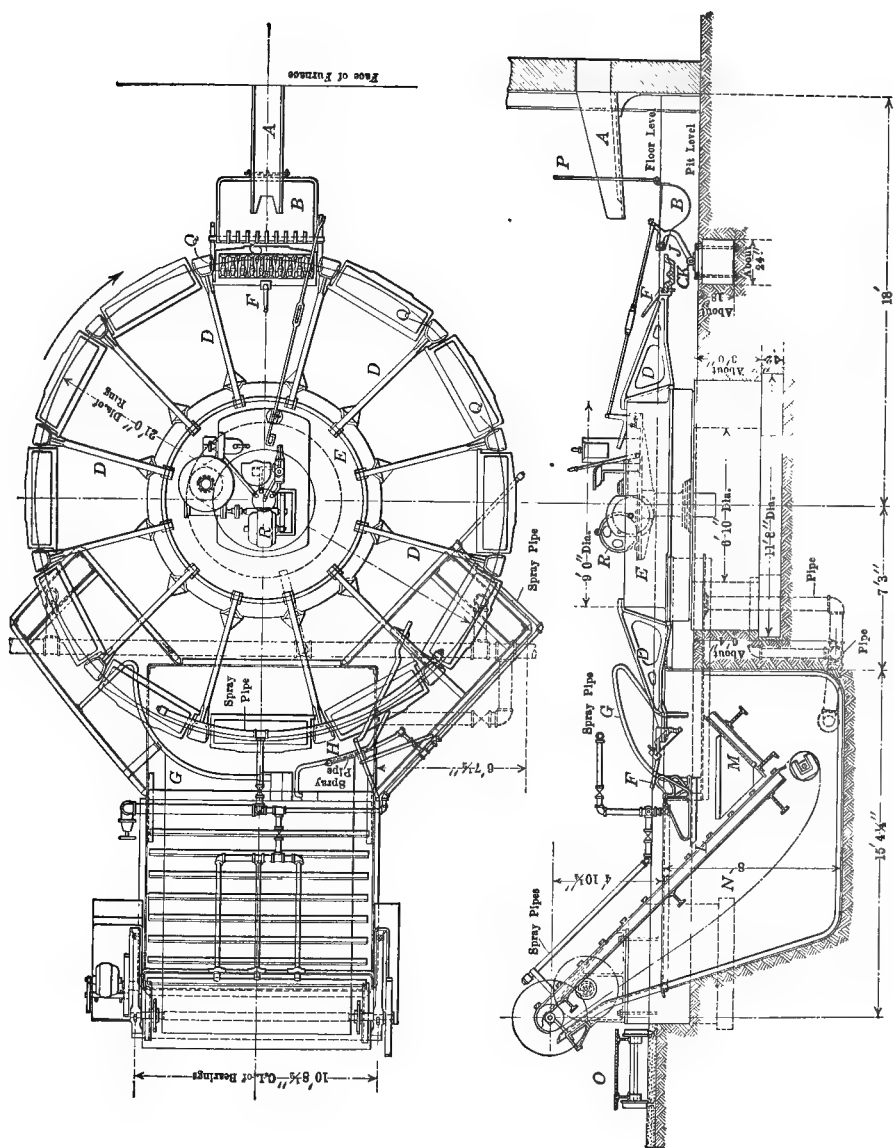
Prior to about 1895 all copper was cast by ladling, and a good deal of copper is still cast in this way. In order to permit increasing the size of a furnace another means of removing the copper had to be devised. In 1895, W. H. Peirce tapped copper from the furnace into ladles,<sup>2</sup> holding about 200 lb., which were suspended from an overhead trolley, moved horizontally by hydraulic power, raised by compressed air, and otherwise manipulated by two men. The flow of copper from the furnace was regulated by plugging the tap-hole. This difficulty and the splashing of the metal while pouring, which caused it to adhere to the molds (cold sets), were the reasons for abandoning this method of casting the finished product.

In 1897 A. R. Walker constructed his casting machine, Figs. 425 and 426, which is in use at many refining plants. The metal is drawn off gradually from the surface of the bath at the end or the side of the furnace. In the brickwork there is left open a tapping-slot, Figs. 400-404, 405-410, 425-426, which is filled by ramming a mixture of raw clay and ground brick, or sand and coke, which will be hard enough to withstand the pressure on the inside, but soft enough to allow cutting a gutter to draw off the copper. For safety, this breast is tamped against, and held in place by transverse iron bars, 1 in. square and 16 in. long, placed either on top of one another or spaced about 2 in. apart, and held by guide-shaped lugs cast in the end or side plates of the furnace. The copper is run from the furnace through a one- or two-spout trough, *A*, lined with a mixture of cement, clay, and sand, into a suspended ladle, *B*, lined with cement and sand and painted with bone-ash, and thence through as many spouts as

<sup>1</sup> Walker: Rio Tinto Works at Port Talbot, Wales, *Eng. Min. J.*, 1907, LXXXIV, 111.

<sup>2</sup> Illustration, *Min. Ind.*, 1898, VII, 253.





FIGS. 425-426.—Walker casting machine.

there are molds (nine in the figure), into tilting molds, *C*, held in a frame, resting on radial arms, *D*, of turntable, *E*.

Ladle, *B*, rests near the front with trunnions, *J*, on curved supports attached to a rocking shaft, *K*, which allows moving forward for pouring and backward for clearing, while table, *E*, is rotated; it is raised at the back by hydraulic power, *P*, for pouring, and lowered for clearing.

The frame holding the tilting molds, *C*, has trunnions, *Q*, resting in recesses at the ends of the cast-iron arms, *D*, to permit inverting of molds and dumping of copper. The trunnions are placed in front of the center of gravity so that the rear flange of a mold will rest on the cross-bar of an arm. The radial arms, *D*, are hung from the turntable, *E*, and are made adjustable to suit larger and shorter molds, which make a complete ring. The turntable, *E*, is revolved in a circular path on rollers by a motor, *R*. The three motions, moving and raising of ladle, *B*, and rotating of table, *E*, are controlled by one man on a stationary platform in the center of *E*, by means of two levers and a rheostat.

In casting wire-bars, two molds replace the nine ingot-molds shown in the drawing, and a two-spout ladle the one with nine spouts; the table is moved slowly while the molds are being filled.

In casting plates or anodes, a single mold replaces the set of ingot-molds; the machine stands still while the metal is poured from a ladle having three spouts.

The cast copper cools while the filled molds travel from ladle, *B*, to water-bosh, *N*. With wire-bars and plates or anodes, the cooling is hastened by blowing compressed air onto the metal. As a mold approaches the water-bosh, its tipping arm, *F*, rises on an inclined bar, *G*, which raises it and turns it over that it may fall against a rest whereupon the casting is dumped from the inverted mold onto the grating, *M*, in water-bosh, *N*, where, sliding down, it is caught by the arms of the conveyer, *L*, raised, and discharged on to car, *O*. As the table, *E*, travels along its circular path, the inverted arm is raised in the same manner by a second inclined bar, *H*, and the mold righted. This is now white-washed with bone-ash, and dries before it returns to the spout, *B*.

A machine casts per hour 65,000 lb. anodes, or 53,000 lb. wire-bars, or 50,000 lb. ingots. The labor required is: 1 furnace-man, 1 machine man, 2 helpers, 1 boy for painting molds with bone-ash; the power is 2.64 k.w.

THE CLARK CASTING MACHINE of the Raritan works, Perth Amboy, N. J., resembles in its general features the machine of Walker; one characteristic is that the wire-bar molds are placed radially instead of tangentially, and can therefore be made of any length desired.

THE LINK-BELT or straight-line casting machine of C. H. Repath is in operation at several smelting and refining plants for casting wire-bars and anodes. It consists<sup>1</sup> essentially of a series of copper molds carried by an endless link-belt in front of a pouring ladle similar to that in the Walker machine. The molds, which receive the metal at one end, are mounted on four-wheel carriages; the front pair of wheels travels on one set of rails, the back on another, so that the inclination of the mold is governed by that of the rails. A wire-bar mold

<sup>1</sup> *Min. Ind.*, 1900, IX, 273.

arriving before the spout is filled from one end while in a horizontal position, is lowered in the same position into a water-bosh, remains there long enough for the metal to solidify, is removed from the water, moved up an inclined plane over the driving head, and the bar then dumped onto a truck. The mold is painted with a bone-ash emulsion on its return path and dries before it arrives underneath the spout to be refilled. Blowing with preheated air hastens the drying.

In casting anodes, the water-bosh is omitted, and the metal cooled by a water-spray. In order to prevent the anode from sticking to the mold, the latter has a pin which automatically forces out the anode from below, whereupon, after passing the driving-head, it is dumped on to a pair of suspended arms, to be trimmed and then removed by tongs suspended from a traveling suspended air-hoist to the anode carriage.

A conveyer handles 50,000 lb. anodes per hour with an expenditure of 17 h.p.

The casting machine in use at Great Falls has been discussed on page 319. A tilting reverberatory furnace is in operation at Tacoma.<sup>1</sup> Tilting oil-heated furnaces at El Paso, Tex., Hayden, Ariz., and other places remove the converter copper and deliver it to a casting machine. The cost of melting, refining and casting cathodes into ingots is in Eastern refineries about \$3.50 per ton of ingot.

MELTING CATHODES.—A new method of melting cathode copper has been developed by L. Addicks and A. Marks,<sup>2</sup> at the works of the United States Metals Refining Co., Chrome, N. J. The essential feature of it is that stacks of cathodes are added from time to time with a charging machine (p. 381), to the molten bath of copper while the casting is going on. A furnace, *e.g.*, receives 340,000 lb. cathodes; these are melted, fined, (making 10,000 lb. slag) and poled in about 18 hr., and leave 330,000 lb. copper in the furnace. This is cast at the rate of 70,000 lb. per hour. Half an hour after the beginning of the cast, 40,000 lb. cathodes are charged; after three-quarters of an hour, 40,000 lb. are again introduced; and after a lapse of an additional hour and one quarter, the third addition of 40,000 lb. is made. In  $2\frac{1}{2}$  hr. 175,000 lb. copper have been cast, leaving in the furnace 275,000 lb., which are now drawn off into the molds in about 4 hr. Thus in  $24\frac{1}{2}$  hr., 450,000 lb. of copper are treated and cast instead of 330,000 lb. in  $22\frac{1}{2}$ – $22\frac{3}{4}$  hr. While casting, the fire has to be kept up, and the metal poled occasionally, when the set shows signs of the copper becoming too low.

<sup>1</sup> Willey, *Eng. Min. J.*, 1906, LXXXII, 146.

<sup>2</sup> U. S. Patent, No. 980584, January 3, 1911.

## CHAPTER VIII

### LEACHING OF COPPER

#### A. LEACHING COPPER ORE

**195. Leaching Copper Ores in General.**<sup>1</sup>—Leaching, as stated in § 42, is suited for low-grade ore with finely disseminated copper mineral and a gangue that is not attacked by the solvent. The simplest case is the one in which the copper occurs as water-soluble sulphate; the ore is also readily amenable to solvents if the copper is present in the form of oxide or carbonate; with sulphide ore the matter is different, as sulphide copper minerals are not sufficiently attacked by the ordinary solvents, and therefore have to undergo a preliminary treatment in order to render them soluble. This is done by converting them into sulphate, or oxide, or chloride.

**196. Solvents.**—The leading solvents are  $H_2O$ ,  $H_2SO_4$  and  $HCl$ ; in second order come  $H_2SO_3$ ,  $Fe_2(SO_4)_3$ , and solutions of  $MetCl_x$ ,  $NH_3$  and  $NH_3$ -compounds; electrolytic extraction has also been tried.

**$H_2O$ .**—The solubilities of the various copper compounds in water have already been given on pp. 56 and 59.

**$H_2SO_4$ .**—This quickly dissolves melaconite, azurite, malachite, and more slowly chrysocolla; cuprite is decomposed into  $CuO$  and  $Cu$ ; an ore carrying cuprite has to be oxidized (weathering, roasting) before treatment.  $H_2SO_4$  does not readily attack  $Fe_2O_3$ . Hot dilute solutions of  $Fe_2(SO_4)_3$  and especially of  $FeSO_4$  are likely to form basic salts which contaminate the copper liquors.  $H_2SO_4$  has the advantage of permitting ready shipment in steel tanks.

**$HCl$ .**—This is a stronger solvent than  $H_2SO_4$ , hence the solutions will be more charged with foreign matter than when  $H_2SO_4$  is used; insoluble oxychlorides are less readily formed than basic sulphates.  $HCl$ -solutions charged with  $MetCl_x$  are solvents for  $Cu_2Cl_2$  and  $AgCl$ . As  $HCl$  cannot be readily shipped, it can be used only near the sources of production, *i.e.*, chemical plants or metallurgical works carrying on chloridizing roasting.

<sup>1</sup> Bode, *Dingl. Polyt. J.*, 1879, CCXXXI, 254, 357, 428.

Douglas, *Min. Res. U. S.*, 1882, 271;

Collins, *Instit. Min. Met.*, 1893-94, II, 4.

Ch. DeFrance, "Extraction du Cuivre, de l'Argent et de l'Or par la Voie Humide," Baudry, Paris, 1897.

Eissler, M., "Hydrometallurgy of Copper." Crosby, Lockwood and Son, London, 1902.

Truchot, P., "Les Pryites," Dunod-Pinat, Paris, 1907.

Greenawalt, W. E., "The Hydrometallurgy of Copper," McGraw-Hill Book Co., New York, 1912.

W. L. Austin, *Min. Meth.*, 1910-11, II, 5, 31, 69, 121, 135, 153, 187, 211, 241, 257, 281; 1911-12, III, 339, 355, 368, 381, 403, 433, 465, 474, 497, 531, 554.

$H_2SO_3$ .<sup>1</sup>— $H_2SO_3$  readily dissolves oxide copper minerals with the exception of  $Cu_2O$ <sup>2</sup> as is the case with  $H_2SO_4$ ; thus  $CuO + H_2SO_3 = CuSO_3 + H_2O$ , but  $CuSO_3$  is unstable;  $3CuSO_3 + CuO = (Cu_2SO_3 + CuSO_3) + CuSO_4$ , being changed slowly into a mixture of cupro-cupric sulphite and cupric sulphate; the former, slightly soluble in  $H_2O$  and readily so in solutions containing  $H_2SO_3$  or  $CuSO_4$ , is decomposed when heated under pressure, viz.;  $Cu_2SO_3 + CuSO_3 = 2Cu + CuSO_4 + SO_2$ . The solvent  $H_2SO_3$  forms the basis of the Neill, Van Arsdale, and the other processes.

$Fe_2(SO_4)_3$ .—This salt (see also Siemens-Halske process, § 218) attacks Cu, its oxide, as well as its sulphide:  $Cu + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4$ ;  $3CuO + Fe_2(SO_4)_3 = 3CuSO_4 + Fe_2O_3$ ;  $Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S$ . Austin<sup>3</sup> found at Cananea that  $ZnS$  was readily attacked,  $Cu_2S$  slowly, and  $CuFeS_2$  hardly at all. Thomas,<sup>4</sup> who examined systematically the behavior of  $Fe_2(SO_4)_3$  came to similar results; he ascertained (1) that the presence of much  $FeSO_4$  affected unfavorably the dissolving power of  $Fe_2(SO_4)_3$  for  $Cu_2S$ ; (2) that dead-roasting sulphide produced oxide not readily attacked, and that therefore the decomposition ought to resemble a sulphatizing roast and be carried on between 450 and 480° C.; and (3) that the grain size need not be smaller than 60-mesh. Abdock<sup>5</sup> found at Rio Tinto that one-half of the Cu in the pyrite could be quickly extracted by  $Fe_2(SO_4)_3$ . A weak point in the use of  $Fe_2(SO_4)_3$  lies in the fact that the  $FeSO_4$  formed has to be regenerated. For the complete regeneration,  $2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O$ , fresh  $H_2SO_4$  has to be added to the charge, as aeration alone of a warm solution,  $10FeSO_4 + 5O = 3Fe_2(SO_4)_3 + Fe_4SO_9$ , causes a loss of 40 per cent. of the iron in the form of basic salt. The choice between the two methods is governed by the cost of the two materials required in the process, 10 lb.  $FeSO_4$  against 2 lb.  $H_2SO_4$  of 66° Bé. Other researches are those of Millberg<sup>6</sup> and DeKay Thompson.<sup>7</sup>

$FeCl_2$ .—This forms the basis of the Hunt-Douglas process I (§ 223). It acts upon copper oxides as follows:  $3Cu_2O + 2FeCl_2 = 2Cu_2Cl_2 + Cu_2 + Fe_2O_3$  and  $3CuO + 2FeCl_2 = Cu_2Cl_2 + CuCl_2 + Fe_2O_3$ , hence  $Cu_2O$  has to be absent, or, if present, has to be first converted into  $CuO$ . As  $Cu_2Cl_2$  is insoluble in  $H_2O$ , but soluble in brine,  $FeCl_2$  dissolved in brine will extract the  $CuO$  from the ore and cause the precipitation of  $Fe_2O_3$ .

$Fe_2Cl_6$  is the reagent used in the Dönnisch process (§ 221) to dissolve copper sulphides, viz.,  $Cu_2S + Fe_2Cl_6 = Cu_2Cl_2 + 2FeCl_2 + S$ , and  $Cu_2S + 2Fe_2Cl_6 = 2CuCl_2 + 4FeCl_2 + S$ . Froehlich<sup>8</sup> found that in his leaching apparatus (p. 433) chalcocite was readily decomposed, that chalcopyrite if given a slight oxidizing roast (see above; § 214 and foll.) yielded nearly all of its copper, and that

<sup>1</sup> Austin, *Min Meth.*, 1911, II, 241.

<sup>2</sup> Jennings, *Eng. Min. J.*, 1908, LV, 822.

<sup>3</sup> *Min. Meth.*, 1910, II, 5.

<sup>4</sup> *Metallurgie*, 1904, I, 8, 39, 59.

<sup>5</sup> *Min. Ind.*, 1900, IX, 235.

<sup>6</sup> *Min. Ind.*, 1906, XV, 292.

<sup>7</sup> *Electrochem. Ind.*, 1904, II, 225.

<sup>8</sup> *Metallurgie*, 1908, V, 206.

tetrahedrite gave up only 34 per cent. of its Cu. Stokes<sup>1</sup> ascertained that enargite was not attacked.

$\text{CuCl}_2$ , used in the Hoepfner process (§ 232) acts upon Cu, Ag, and their sulphides:  $\text{Cu} + \text{CuCl}_2 = \text{Cu}_2\text{Cl}_2$ ,  $\text{CuS} + \text{CuCl}_2 = \text{Cu}_2\text{Cl}_2 + \text{S}$ ,  $\text{Cu}_2\text{S} + 2\text{CuCl}_2 = 2\text{Cu}_2\text{Cl}_2 + \text{S}$ ;  $\text{Ag}_2 + 2\text{CuCl}_2 = 2\text{AgCl} + \text{Cu}_2\text{Cl}_2$ ,  $\text{Ag}_2\text{S} + 2\text{CuCl}_2 = 2\text{AgCl} + \text{Cu}_2\text{Cl}_2 + \text{S}$ . On account of the insolubility in  $\text{H}_2\text{O}$  of the  $\text{Cu}_2\text{Cl}_2$  formed, the  $\text{CuCl}_2$  has to be dissolved in brine;  $\text{Cu}_2\text{Cl}_2$  has a powerful chloridizing effect upon sulpharsenide and sulphantimonide silver minerals (Kröhnke process).

$\text{NH}_3$  and some of its salts are solvents for copper. Thus, Cu,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , O form  $\text{CuO} \cdot x\text{NH}_3$  a blue solution;  $\text{H}_2\text{CuO}_2$  is readily soluble in  $\text{NH}_3 \cdot \text{H}_2\text{O}$ ; CuO is insoluble in  $\text{NH}_3$ , but soluble if this contains some ammonia salt, e.g.,  $\text{NH}_4\text{HCO}_3$ , forming a double salt  $\text{CuCO}_3 \cdot x\text{NH}_3$ ;  $\text{Cu}_2\text{O}$  is readily soluble forming a colorless solution which turns blue upon exposure to air;  $\text{Cu}_2\text{S}$  is readily attacked,  $\text{Cu}_2\text{S} + \text{O} + \text{NH}_3 + n\text{H}_2\text{O} = \text{H}_2\text{Cu}_2\text{O}_2 + \text{S} + \text{NH}_3 + (n-1)\text{H}_2\text{O}$ . The action of  $\text{NH}_4$  is slow unless an oxidizing agent (air,  $\text{MnO}_2$ ,  $\text{CaClO}_2$ ), is present; the gas is readily recovered from copper solutions by distillation. The use of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  charged with some  $\text{NH}_4$ -salt as solvent seems to be suitable with an ore having a gangue (calcareous) that is readily attacked by acids. Ammonia liquor has been frequently suggested<sup>2</sup> and used for the treatment of oxide copper ores, but has not been quite successful because  $\text{NH}_3$  was retained by the ore, the apparatus being imperfect, and the cost of treatment too high. As at present the cost of  $\text{NH}_4$ -salts is less, and the difficulty with apparatus has been overcome, there is possibly a new field for the solvent.

*Direct electrolytic solution* of copper from raw and roasted ores has been tried, but has proved a failure, if for no other reason than the imperfect electric contact shortly after the process has been started.

**197. Precipitants.**—From its solutions copper is precipitated mainly by Fe,  $\text{FeS}$ ,  $\text{H}_2\text{S}$ , and  $\text{SO}_2$ -gas; solutions of  $\text{CaS}_5$ ,  $\text{Na}_2\text{S}$ , and emulsions of  $\text{H}_2\text{CaO}_2$  have been tried. Electrodeposition using an insoluble anode has come into use in recent years. All solutions have to be clarified before the copper is precipitated nor ought they to be too concentrated.

*Fe.*—The purer the iron and the finer its state of division, the more energetic is the action; hence ground iron sponge with 70 per cent. Fe produced by the reduction of purple ore<sup>3</sup> (§ 232) acts the quickest; then follow, in the order given, wrought iron, gray iron, steel, white iron. Wrought iron furnishes a coarse precipitate, gray iron spongy copper, white iron a metal that is more coherent than that from gray iron. In practice ordinarily the cheapest available scrap, including the tin can, serves to recover copper. According to  $\text{CuSO}_4 + \text{Fe} = \text{Cu} + \text{FeSO}_4$  and  $\text{Cu}_2\text{Cl}_2 + \text{Fe} = 2\text{Cu} + \text{FeCl}_2$ , 88.8 or 44.4 lb. Fe are required for 100 lb. Cu. In practice  $2 \pm$  lb. Fe are consumed per pound of Cu

<sup>1</sup> *Econ. Geol.*, 1907, II, 23.

<sup>2</sup> *Berg. Hüttenm. Z.*, 1852, XI, 799; Barruel, 1860, XIX, 111; Strohmeyer, 419; Bischoff, 1862, XXI, 140; "Commern Works," 230; Jung, 1868, XXVII, 414; Summary—*Zt. Berg. Hütten. Salin. Wesen i. P.*, Schnabel, 1880, XXVIII, 262; also Schnabel-Louis, "Handbook of Metallurgy," 1905, I, 679.

<sup>3</sup> Lunge, *op. cit.*, I<sup>3</sup>, p. 1505.

with a cupric salt owing to the formation of basic ferric salts and the liberation of free acid or ferric salt. This is especially the case with  $\text{H}_2\text{SO}_4$  as solvent ( $2\text{FeSO}_4 + \text{H}_2\text{O} + \text{O} = \text{Fe}_2\text{SO}_6 + \text{H}_2\text{SO}_4$  or  $6\text{FeSO}_4 + 3\text{O} = 2\text{Fe}_2(\text{SO}_4)_3 + \text{Fe}_2\text{O}_3$ ), less so with  $\text{HCl}$ : ( $6\text{FeCl}_2 + 3\text{O} = 4\text{FeCl}_3 + \text{Fe}_2\text{O}_3$ ).

In order to diminish the consumption of Fe, Zoppi<sup>1</sup> reduced  $\text{Fe}_2(\text{SO}_4)_3$  to  $\text{FeSO}_4$  by means of  $\text{SO}_2$ -gas generated in a kiln:  $\text{Fe}_2(\text{SO}_4)_3 + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$ . At the same time he reduced  $\text{As}_2\text{O}_5$  to  $\text{As}_2\text{O}_3$ , which was precipitated by Fe and later separated from the Cu by washing. The  $\text{H}_2\text{SO}_4$  formed in the reduction dissolved some Fe, but less than the  $\text{Fe}_2(\text{SO}_4)_3$  in the original solution. At Rio Tinto<sup>2</sup>  $\text{Fe}_2(\text{SO}_4)_3$ -solutions are passed over ore heaps, and  $\text{FeS}_2$  reduces them to  $\text{FeSO}_4$  as shown by  $7\text{Fe}_2(\text{SO}_4)_3 + \text{FeS}_2 + 8\text{H}_2\text{O} = 15\text{FeSO}_4 + 8\text{H}_2\text{SO}_4$ . Neutralization of free  $\text{H}_2\text{SO}_4$  with  $\text{H}_2\text{CaO}_2$  has been suggested, whereby  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{SO}_6$  would be precipitated with some  $\text{CaSO}_4$ , and the solution at the same time clarified.

In order to hasten the precipitation by Fe, Patera,<sup>3</sup> later Peck,<sup>4</sup> and more recently Austin<sup>5</sup> have proposed the addition of coke,<sup>6</sup> as the coke-iron couple formed causes Cu to fall out more quickly and more completely than when Fe is used alone; the formation of basic salts is also diminished, but the action of Fe upon  $\text{Fe}_2(\text{SO}_4)_3$  is also rendered more energetic, so that the liquor freed from Cu has to be removed from the vat as quickly as possible. High vertical tanks with entrance for Cu-bearing liquor at the bottom and discharge for Cu-free liquor at the top are recommended. The tank of Fröhlich (§ 221) is advocated by Austin.

OTHER REAGENTS.<sup>7</sup>— $\text{FeS}^8$  precipitates Cu from  $\text{CuSO}_4$ ;  $\text{H}_2\text{S}$ ,<sup>9</sup> generated by several processes, has been used and the  $\text{CuS}$  separated by filter-pressing.

$\text{SO}_2$  acting under pressure upon a copper salt heated in a closed vessel causes Cu to separate:  $\text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O} = \text{Cu} + 2\text{H}_2\text{SO}_4$ ; the process has been patented by Juman.<sup>10</sup>

$\text{CaS}_5$ - and  $\text{Na}_2\text{S}$ -solutions have been suggested and their advantages in not precipitating As and Sb urged.

$\text{H}_2\text{CaO}_2$  gives a bulky precipitate of  $\text{H}_2\text{CuO}_2$  or  $\text{Cu}_2\text{O}$  mixed with  $\text{H}_6\text{Fe}_2\text{O}_6$  difficult to handle; in sulphate solutions  $\text{CaSO}_4 + \text{aq}$  falls out at the same time.

In the electrodeposition of Cu from aqueous solutions using insoluble electrodes, Cu is plated on the cathode, while  $\text{SO}_4$  or Cl is set free at the anode. Several attempts have been made to utilize the energy of the  $\text{SO}_4$ - or Cl-anion by having it act chemically upon the electrolyte surrounding the anode and bringing it back to its original higher state of oxidation or chlorination, and to

<sup>1</sup> *Ann. Mines*, 1876, IX, 190; *Berg. Hüttenm. Z.*, 1876, XXXV, 363.

<sup>2</sup> *Abdock, Min. Ind.*, 1900, IX, 234.

<sup>3</sup> *Dingl. Polyt. J.*, 1867, CLXXXIV, 134.

<sup>4</sup> *Oest. Zt. Berg. Hüttenw.*, 1880, XXVIII, 613, 626.

<sup>5</sup> *Min. Melh.*, 1911, II, 120.

<sup>6</sup> *Slaughter, U. S. Patent*, No. 1001466, Aug. 22, 1911.

<sup>7</sup> *Kerl, B.*, "Metallhüttenkunde," Felix, Leipsic, 1881, p. 243.

<sup>8</sup> *Croasdale, Eng. Min. J.*, 1914, XCVII, 745.

<sup>9</sup> *Buddëus, Berg. Hüttenm. Z.*, 1904, LXIII, 73.

<sup>10</sup> *Eng. Min. J.*, 1908, LXXXVI, 133.

thus neutralize to a large extent the counter-electromotive force that would have to be overcome otherwise.<sup>1</sup> With sulphate solutions, SO<sub>2</sub>-gas has been introduced at the anode (Carmichael process, § 206), so that the O, set free by the action of the acid radical SO<sub>4</sub> upon H<sub>2</sub>O (viz., SO<sub>4</sub>+H<sub>2</sub>O=H<sub>2</sub>SO<sub>4</sub>+O), may be removed, and thus its counter-electromotive force at the anode not only more or less neutralized, but some of the H<sub>2</sub>SO<sub>4</sub>, lost in the leaching, restored. In the Laszczynski process (§ 205), the O is allowed to pass off, but the FeSO<sub>4</sub> is prevented from being converted into Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> by enclosing the anode in a bag.

**198. Leaching Apparatus and Method.**—The leaching vats used are commonly of wood, tarred or rarely lead-lined; they are also built of acid-proof brick and asphalt-concrete.

The liquors are elevated<sup>2</sup> by means of acid-eggs, air-lift pumps, reciprocating and centrifugal pumps, and perhaps screw-conveyors.

The method of leaching is usually that of percolation; mechanical stirring of ore or circulation of solvent is found occasionally;<sup>3</sup> revolving barrels are the exception on account of excessive cost. The counter-current system of continuous leaching, adopted from the treatment of gold ores with potassium cyanide, is being tried upon acid-treatment of copper ores, and promises to be successful.

The operation of leaching, when conducted systematically, is such that only rich solutions go to the precipitating vats; fresh or only slightly charged solvents are passed over nearly exhausted ore; and partly saturated solutions, over fresh ore (counter-current principle).

For filtering, false bottoms covered with suitable filtering media are common; filter-presses or suction-filters are used mainly for precipitated copper.

**199. Precipitating-Vat and -Method.**—The precipitating vats are usually of wood. With stationary vats, the copper liquor is made to pass through a series of tanks, or to circulate in a single tank, or to flow through long troughs arranged in step-form.

Precipitation may be accelerated in stationary vats by mechanical stirring or circulation, or by the use of revolving barrels.

The precipitated copper is usually contaminated with impurities. A pulverulent precipitate may have to be washed before it is dried and smelted in a reverberatory furnace for blister copper or for matte, according to its character.

**200. Outline of Leaching Processes for Ore.**—The subject of leaching copper ore will be treated under the following main headings:

#### I. Sulphate Ore.

##### 1. Mine Water.

##### 2. Tailing and Dump.

<sup>1</sup> Processes of Siemens-Halske, § 218; Hoepfner, § 222; Greenawalt, § 209.

<sup>2</sup> See Hofman, "General Metallurgy," 1913, p. 687 and following.

<sup>3</sup> *Parral Tank*: Mac Donald, *Eng. Min. J.*, 1914, xcvi, 325, 422; *Met. Chem. Eng.*, 1914, xii, 141.



## II. Oxide Ore.

## III. Sulphide Ore.

## A. Conversion of Sulphide into Sulphate:

1. Weathering.
2. Sulphatizing Roast.
3. With Ferric Sulphate,  $\text{Fe}_2(\text{SO}_4)_3$ .

## B. Conversion of Sulphide into Oxide.

1. Oxidizing Roast.

## C. Conversion of Sulphide into Chloride.

1. With Ferric Chloride,  $\text{FeCl}_3$ .
2. With Cupric Chloride,  $\text{CuCl}_2$ .
3. With Oxidizing Roast and Ferrous (Calcic) Chloride,  $\text{Fe}(\text{Ca})\text{Cl}_2$ .
4. With Chloridizing Roast of
  - (a) Crude ore.
  - (b) Roasted Ore.

**201. Leaching Sulphate Ore.**—Ores in which copper is found as water-soluble sulphate do not occur in sufficient quantity to make their treatment the object of a separate operation. However, old workings of a mine, mine-fillings, and tailing-dumps that have been exposed to the oxidizing influences of air and water furnish waters charged with sufficient  $\text{CuSO}_4$  to pay for the recovery of the Cu.

The mine-waters of Schmoellnitz, Hungary,<sup>1</sup> have been treated for years, as have those of the Rammelsberg mine, Germany;<sup>2</sup> Wicklow, Ireland;<sup>3</sup> Ashio, Japan;<sup>4</sup> and other localities.

In the United States the waters of the Butte mines, Mont.;<sup>5</sup> of the Copper Queen mine, Bisbee, Ariz.;<sup>6</sup> of the Iron Mountain, Cal.;<sup>7</sup> and the tailing-dumps of Butte, Montana; Wallaroo, Australia;<sup>8</sup> Gumeshevsky, Russia<sup>9</sup> furnish examples of modern modes of operating.

**202. Mine-waters.** (I) SCHMOELLNITZ, HUNGARY.—The compositions of the mine-waters, April, 1859, before and after cementation are given in Table 98.

<sup>1</sup> Steinhausz, *Oester. Jahrb.*, 1896, XLIV, 314.

Fähndrich, *Zt. Berg. Hütten. Salin. Wesen. i. P.*, 1898, XLVI, 232; *Berg. Hüttenm. Z.*, 1904, LXIII, 13, 41, 73.

<sup>2</sup> Bräuning, *Zt. Berg. Hütten. Salin. Wesen. i. P.*, 1877, XXV, 132.

<sup>3</sup> Argall, *Min. Sc. Press*, 1906, XCII, 325, XCIII, 111.

<sup>4</sup> Richards, *Tr. A. I. M. E.*, 1912, XLIII, 464.

<sup>5</sup> Edit. *Min. Rep.*, 1905, LII, 618.

<sup>6</sup> Bushnell, *Eng. Min. J.*, 1907, LXXXIII, 1229, *Min. Sc. Press*, 1908, LVII, 530, 1911, CIII, 649.

Probert, *op. cit.*, 1908, XCVI, 27.

Stone, *Eng. Min. J.*, 1908, LXXXVI, 953; Edit. *Met. Chem. Eng.*, 1910, VIII, 614.

Gillie-Sommerfeldt, *Metallurgie*, 1911, VIII, 187.

Febles, *Tr. A. I. M. E.*, 1913, XLVI, 177.

<sup>8</sup> Chittenden, *Eng. Min. J.*, 1908, LXXXVI, 853.

<sup>7</sup> Campbell, *Min. Sc. Press*, 1907, XCIV, 57.

<sup>8</sup> Williams, *Eng. Min. J.*, 1908, LXXXVIII, 58.

<sup>9</sup> Simon, *Tr. Inst. Min. Met.*, 1909-10, XIX, 212; *Min. Ind.*, 1910, XIX, 210.

TABLE 98.—MINE-WATER OF SCHMOELLNITZ, HUNGARY

One cbm. mine-water contains	Contains Kg. of									Total
	FeSO <sub>4</sub>	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Fe	CuSO <sub>4</sub>	Cu	ZnSO <sub>4</sub>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	CaSO <sub>4</sub>	MgSO <sub>4</sub>	
Before cementation	5.86	8.12	4.68	1.43	0.56	0.86	8.81	1.11	5.35	31.54
After cementation	18.17	0.19	6.77	0.08	0.04	0.79	7.94	1.06	5.10	33.33

The waters pass through 12,400 ft. of launders made of boxes 12 ft. long, 12 in. wide, 12 in. deep, which have a fall of 1 in 25, and are charged with cast-iron plates 10 by 2.5 by 0.5 in. The discharge-end of one launder is placed inside of the feed-end of the next following. From the last launder the liquor drops through a chute on to a bed of pig iron, as impact of liquor greatly assists precipitation of copper, and then passes through settling tanks. The iron plates are swept daily; the cement copper is removed fortnightly from the first 40 or 50 launders, in which most of the copper is precipitated, and every three or four weeks from the others; the copper is passed through sieves on its way to collecting tanks, settled, and dried; it assays about 57 per cent. Cu. The iron consumption, 2.5 Fe : 1 Cu, varies with the amount of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> present. It has been noted that the presence of much FeSO<sub>4</sub> is unfavorable to precipitation; when it exceeds a certain percentage no Cu is precipitated, but Fe<sub>2</sub>O<sub>3</sub>·xFe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> separates. The presence of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> favors the precipitation of copper.

(2) BUTTE, MONT.—The recovery of copper from the mine-waters of Butte began in 1888, was put on a business basis in 1901, and has increased to such an extent that the monthly production has reached 275 tons. The waters having a temperature of 25–30° C. contain from 0.0075 to 0.1150, average 0.0500 per cent. Cu, and from 0.001 to 0.0008 per cent. free SO<sub>3</sub>. Two kinds of apparatus are in use for precipitation, forming the so-called flume- and the tower-systems; a combination of the two is also in operation.

The flumes are boxes of 1–1.5-in. boards, 3–4.5 ft. wide, 12–14 in. deep and 800–2000 ft. long, having a fall ranging from 1.3 to 3.75 per cent.; the grade toward the end of a system is greater than at the beginning, as the smaller the amount of Cu the water contains, the more ready is the attack of the iron; the velocity of the water is 50–70 ft. per minute with a depth of 6–12 in.; two or three rows of flumes are often placed side by side. Scrap iron and tin cans are used as precipitants. Scrap iron, such as rails, pipes, bars, is placed lengthwise on the bottom near the inflow, short transverse pieces separating the layers; small scrap is distributed lower down in the flume, as are tin cans; these have to be freed from paper and grease (burnt off); 1000 ft. of flume hold about 75 tons of iron and require daily about 1000 lb. fresh iron; 1.1–2.0 lb. Fe are consumed per 1 lb. Cu; the Cu is swept off the Fe every 2 hr. during the day; it collects in communicating settling-tanks; a clean-up is made every two to six weeks, when the larger pieces of remaining iron are shaken and scraped, smaller ones raked over. The liquor from the settling tanks is drained; the precipitate is shoveled out, air-dried to 8–15 per cent. H<sub>2</sub>O, and shipped; it

contains Cu 60-70 and Fe 8 per cent. An analysis given by Febles<sup>1</sup> shows H<sub>2</sub>O 12.2, Cu 70.9, SiO<sub>2</sub> 2.3, FeO 8.4, Al<sub>2</sub>O<sub>3</sub> 2.9, CaO 0.3, S 0.8, As 0.27. The ratio As:Cu in the water from the Leonard mine is 1:189; that in cement copper 1:509, showing that only part of the As is precipitated. The recovery of Cu is from 90 to 98 per cent.

FLUMES are convenient for charging and manipulating; it is generally held that the precipitation with them is more effective than with towers.

TOWERS are heavy wooden frames, 40-70 ft. long, 15-30 ft. high, 6-10 ft. wide, with wooden stringers, 2 by 4 in., placed lengthwise, 3 in. apart, to form floors, 18 in. distant from one another which carry the precipitating iron. Baffle boards are nailed to the sides and ends to prevent the falling water from splashing. In some instances the stringers are omitted, and the tower is charged with scrap that is too large for the flumes. A distributing flume delivers the mine-water over the top of the tower. Beneath the towers are communicating settling tanks which can be disconnected for cleaning. The mine-water is raised by bronze (85 Cu, 15 Sn) centrifugal pumps to the top of a tower and distributed. It falls evenly over the iron, which is kept more or less clean by the fall of the water, but requires beating or scraping to dislodge the copper.

The clean-up is similar to that of the flumes. The copper precipitate and the decopperized water contain mixtures of ferric hydrate and basic ferric sulphate going under the general name of "ochre,"<sup>1</sup> which shows upon analysis, SiO<sub>2</sub> 3.11, CuO trace, Al<sub>2</sub>O<sub>3</sub> 1.71, Fe<sub>2</sub>O<sub>3</sub> 66.72, ZnO trace, Mn<sub>2</sub>O<sub>3</sub> none, CaO none, MgO none, SO<sub>3</sub> 11.51, H<sub>2</sub>O 16.95 (calculated for limonite). The rational analysis would give SiO<sub>2</sub> 3.11, Al<sub>2</sub>O<sub>3</sub> 1.71, 2Fe<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O (limonite) 59.95, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·Fe<sub>2</sub>O<sub>3</sub>+8H<sub>2</sub>O 35.23 (basic ferric sulphate).

Figs. 427-428 give a plan and section of the High-Ore precipitating plant<sup>2</sup> which treats per minute about 1200 gal. water of 30° C. containing about 0.0500 per cent. Cu. The water enters three flumes, 4 ft. wide by 2 ft. deep with a 2 per cent. grade, and travels to the first settlers 300 ft. distant. The flumes are charged with rails, pipes, rods, and bars, which are frequently turned over to separate the cement copper and leave a clean precipitating surface. Every few days, one flume is cut out for cleaning, the iron is removed, and the precipitate washed into the settler. After the first settling tank, the flumes are widened to 6 and 8 ft., and the grade is increased to 2½ per cent. The settling tanks are spaced 75 ft. apart, for the next 500 ft. These 800 ft. of flume form the first unit; in it the flow of water is about 60 ft. per minute.

The settling tanks are wooden boxes, 15 ft. long by 8 ft. deep, built into the flume. When about filled with precipitate, this is sluiced through troughs into three connecting settlers for collection; the clear water is siphoned off, and the cement copper air-dried.

From the first unit the water enters the first tower, 129 by 8 ft. and 19 ft. high, with attached settler and charged with large scrap not suited for the flume; then a second tower, 129 by 8 ft. and 19 ft. high. It travels thence in 6 min.

<sup>1</sup>Loc. cit.

<sup>2</sup>Febles, loc. cit.





through a double flume, 300 ft. long with a 1.3-per-cent. grade and charged with tin cans and small scrap, drops through a tower, 81 by 11 ft. and 25 ft. high, and four smaller ones, 8-9 ft. high. From the last tower the water enters a settler, 27 by 28 ft. and 4 ft. deep, and then goes to waste. Table 99 gives analyses of the head- and tail-water of the High-Ore mine; Table 100 furnishes the leading facts of the three mine-water precipitating plants of Butte.

TABLE 99.—ANALYSES OF HEAD- AND TAIL-WATER HIGH-ORE PRECIPITATING PLANT, BUTTE

	SiO <sub>2</sub>	CuO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	ZnO	CaO	MgO	SO <sub>3</sub>	Cl	Total, per cent.
Head-water...	0.0504	0.6683	0.2102	0.5931	0.2194	0.0714	0.6969	0.3224	0.1200	3.5246	0.0724	6.5491
Tail-water...	0.0384	0.0125	0.1926	0.0729	1.0427	0.0574	0.4679	0.3296	0.1376	2.7614	0.0862	5.1959

TABLE 100.—WORKINGS OF THREE MINE-WATER PRECIPITATING PLANTS, BUTTE, MONT.

	High-Ore plant	Leonard plant	Silver-Bow plant
Total length of flumes (excluding towers), feet....	1,769	1,943	805
Total fall, feet.....	180	87	56
Average fall per 100 ft., feet.....	10.25	5.6	7
Total height of towers, feet.....	100	38	20
Total length of towers, feet.....	630	224	25
Average width of towers, feet.....	11.45	12.7	7
Total area of towers, square feet.....	7,213.5	2,315.0	175.0
Average width of flumes, feet.....	12.5	5.7	4.9
Total area of flumes, square feet.....	22,169	13,400	3,908
Average temperature of water entering, ° C.....	29	36	24
Average temperature of water leaving, ° C.....	12	11	17
Average flow of water, gallons per minute.....	1,200	1,500	356
Average velocity in flumes, feet per minute.....	70.8	61	50.25
Total time of contact, minutes.....	26.5	29	16
Average copper-content entering, per cent.....	0.0516	0.0482	0.0748
Average copper-content leaving, per cent.....	0.0010	0.0020	0.0082
Copper extracted, per cent.....	98.6	95.85	90.37
Total length of settlers, feet.....	938	1,150	128
Average width of settlers, feet.....	11.31	7.65	9.3
Total area of settlers, square feet.....	10,613	7,781	1,188
Total precipitating area, square feet.....	29,382	15,725	4,300

The cost at the Leonard plant per pound Cu produced is: Labor, \$0.0352; supplies and iron, \$0.0140; sundries, \$0.0002; total, \$0.0494.

(3) COPPER QUEEN, BISBEE, ARIZ.—The average amount of mine-water treated in the plant is 8170 gal. per hour; the largest amount handled has been 20,200 gal. The cementation plant consists of a rectangular five-story structure, 78 by 108 ft. and 30 ft. high, in the center of which are four clean-up tanks, 25 by 40 ft. and 2 ft. deep. The outer frames are built of 8 by 8-in. posts; they are joined by 6- by 8-in. stringers which carry five tiers of double rows of precipitating troughs. A trough, made of 2-in. boards, is 3 ft. wide and 20 in. deep, has at intervals of 2.5 ft. cross-pieces, 2 by 4 in., placed 2 in. above the bottom which carry four 1-by 4-in. boards forming a false bottom to support the precipitating iron (tin cans). The space beneath the false bottom serves to collect

the cement copper until ready to be hosed into the settling tanks. The troughs have a fall of 0.25 to 2 in. in 12 ft., the slope increasing as the water grows poorer in copper. The mine-water enters at one corner of the top tier, flows through the two troughs around the rectangle to the corner where it entered, glides down a slide onto the next tier, makes a second circuit, and so on to the bottom, where a flume leads it to settling tanks, 9 by 17 ft. and 9 ft. deep. The 300 gal. mine water delivered per minute (twice as much as stated above) to the plant carry 10 grains Cu per gal., they travel 1650 ft. at an average speed of 15 ft. per minute and give up 90 per cent. of their Cu. Table 101 gives analyses

TABLE 101.—HEAD- AND TAIL-WATER, BISBEE, ARIZ.

	Grains per Gallon						
	Total Fe	FeO	Fe <sub>2</sub> O <sub>3</sub>	CaO	Mn	SO <sub>3</sub>	Cu
Head-water.....	65.0	40.81	24.2	30.2	13.9	319.7	54.8
Tail-water.....	116.6	107.5	9.0	38.0	12.1	323.1	1.1

of the head- and tail-mine-water. The upper three tiers are cleaned every second day by hosing; the lower two less frequently. The precipitated Cu is collected in the settling tanks, settles sufficiently in 2 hr. to permit siphoning off the liquor, is shoveled out and air-dried; it retains 40 per cent. H<sub>2</sub>O when shipped; a dry assay-sample showed Cu 35, SiO<sub>2</sub> 6, Fe 17, Al 13, S 1.5 per cent. Once a month a thorough clean-up is made, when the troughs are emptied as well as the clean-up tanks. The black mud from the latter is bailed out and air-dried in about one month in two drying boxes, 18×25 ft. and 2 ft. deep. Two men are required on a shift; at the monthly clean-up three extra men are necessary.

**203. Mill Tailings and Mine Dumps.** (1) BUTTE, MONT.—The mill tailings of the Montana Ore-Purchasing Co., which carry about 1 per cent. Cu, have become sufficiently weathered to allow recovery of part of the copper by leaching. They cover about 10 acres and rest upon slime which reduces the seepage to about 20 per cent. The surface is divided into two sections; in each are excavated basins arranged in terraces. Tunnels, 800–1200 ft. long, are driven 200 ft. apart on the bed of slime; they are 5 ft. high, 3 ft. wide at bottom and 2 ft. at top, and are well timbered. Acid mine-water, freed from 95 per cent. of its Cu and carrying per liter SiO<sub>2</sub> 0.0992, Cu 0.0025, Al<sub>2</sub>O<sub>3</sub> 0.1241, Fe<sub>2</sub>O<sub>3</sub> 0.1541, FeO 1.5082, MnO 0.0502, ZnO 0.4257, CaO 0.3936, MgO 0.2172, SO<sub>3</sub> 3.5400, Cl 0.0234 g., is delivered by bronze centrifugal pumps to the basins that it may percolate through the tailings; it collects in the tunnels, runs into a sump, and is pumped into precipitating launders. The surfaces of the basins are allowed to dry periodically to remove precipitated iron salts and to assist in the oxidation of sulphide mineral.

(2) WALLAROO, AUSTRALIA.—Here the tailings with 0.9 per cent. Cu are stacked in large heaps, 30–60 ft. high, on specially prepared ground covering an area of 20 acres. One part of a heap is irrigated at a time with mine-water, carrying 100 grains FeSO<sub>4</sub> per gallon with a trace of free acid, and with sea water, while the moistened other part undergoes oxidation; 50 per cent. of the Cu has been recovered so far by leaching.

(3) GUMESCHEVSKY, URAL.—At these works an old dump with Cu 0.75, SiO<sub>2</sub> 37, Fe 19.6, Al<sub>2</sub>O<sub>3</sub> 20, CaO 0.25 per cent. is leached in tanks with H<sub>2</sub>SO<sub>4</sub>; one-third of the ore, in large pieces, is first ground in Chilean mills; the rest goes as a liquid pulp through launders to 10 concrete tanks lined with 1 in. of reinforced concrete. A tank, 184 by 42 by 6.5 ft., holds 200 tons of dry pulp and receives with the necessary water 13.2 tons of H<sub>2</sub>SO<sub>4</sub> of 53° Bé. The pulp is agitated for 9 hr. by traveling mechanical stirrers, and allowed to settle; the copper liquor is decanted, and the pulp then agitated with water four times for 4 hr. The Cu is precipitated on cast-iron plates in 20 asphalt-lined concrete tanks in which the recovery is 95 per cent.; the consumption of iron 1.8–2 Fe : 1 Cu; the cement copper assays 65–75 per cent. Cu; the total recovery is 50 per cent. of the Cu-content in the ore.

**204. Leaching Oxide Ore** (See also § 219).—The leading example of leaching such ores with H<sub>2</sub>SO<sub>4</sub> given in the literature is that of Stadtberge, Germany,<sup>1</sup> but the practice was abandoned long ago.

In the U. S.<sup>2</sup> the Arizona Copper Co., of Clifton, Ariz., leaches with H<sub>2</sub>SO<sub>4</sub> the jig-tailings from a 150-ton concentrator treating oxide ore with a siliceous gangue; the Cu is precipitated with Fe. Much experimental work<sup>3</sup> is carried on at present upon oxide ore in Arizona and other states.

At the plant of the Butte-Duluth Mining Co.<sup>4</sup> or the Bullwhacker works, Butte, Montana<sup>5</sup> oxide ore is leached with H<sub>2</sub>SO<sub>4</sub> and the Cu deposited electrically.

**205. The Laszczynski process,**<sup>6</sup> introduced first at the Miedzianka mine, Kielce-Checing, Poland, and later at the Karkaralinsk mine, Semipalatinsk, Siberia, is a new process for the electro-deposition of Cu from a sulphate solution, using insoluble anodes. In electrolyzing a CuSO<sub>4</sub>-solution, the salt is split into the kation Cu and the anion SO<sub>4</sub>, and the latter is decomposed according to SO<sub>4</sub>+H<sub>2</sub>O=H<sub>2</sub>SO<sub>4</sub>+O. Copper liquors from ores always contain some FeSO<sub>4</sub> which is changed at the anode into Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> according to 2FeSO<sub>4</sub>+SO<sub>4</sub>=Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. This salt has a dissolving effect upon deposited Cu and makes it brittle. As in the process the regenerated H<sub>2</sub>SO<sub>4</sub> is used over and over, the Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> accumulates to such an extent that pretty soon all deposited Cu is re-dissolved. The formation of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is prevented in the new process by enclosing the insoluble Pb anodes,  $\frac{1}{8}$  in. thick, in tight-fitting cotton bags, the thickness of the cotton being in inverse proportion to the strength of current. When such an anode is immersed in the bath, the Cu(Fe)SO<sub>4</sub>-solution is the same inside and outside of the bag; when the circuit is closed the electro-positive

<sup>1</sup> Strohmeyer, *Berg. Hüttenm. Z.*, 1856, xv, 218; Miszke, *Oest. Zt. Berg. Hüttenw.*, 1871, ix, 108; Gerhardt, *Zt. Ver. deutsch. Ing.*, 1872, xvi, 305.

<sup>2</sup> Douglas, *Min. Ind.*, 1897, vi, 230; Correspondent, *Min. Sc. Press*, 1913, cvii, 523.

<sup>3</sup> Correspondent, *Eng. Min. J.*, 1913, xcvi, 650, 962.

Editor, *Op. cit.*, 1914, xcvi, 101.

<sup>4</sup> *Mel. Chem. Eng.*, 1914, xii, 2; *Eng. Min. J.*, 1914, xcvi, 819.

<sup>5</sup> Peterson, *Min. Eng. World*, 1913, xxxix, 423, 584 (Anonym.).

<sup>6</sup> Stoeger, *Oest. Zt. Berg. Hüttenw.*, 1906, liv, 387; *Metallurgie*, 1906, iii, 820; *Rev. Un. Min.*, 1907, xix, 75; *Min. Ind.*, 1907, xvi, 373; Austin, *Min. Meth.*, 1911, iii, 368.



Fe-ions leave the bag and move toward the cathode at a greater speed than the electrolyte diffuses through the bag, hence there is no  $\text{FeSO}_4$  inside of the bag to be converted at the anode into  $\text{Fe}_2(\text{SO}_4)_3$  by the electronegative  $\text{SO}_4$ , and there is no solution of deposited Cu. The surface of the Pb anode will become coated with  $\text{PbO}_2$  which increases the required voltage on account of the resistance it offers to the passage of the current.

At Miedzianka, the copper minerals are chalcocite, azurite, and malachite. The ore assaying from 15 to 45 per cent. Cu, is crushed fine in rolls; mixed with 5 per cent. clay; and briquetted under sufficient pressure to allow charging, without preliminary drying, into the roasting furnace, a small shaft furnace with lateral fire-place treating 10 tons in 24 hr., and converting  $\text{Cu}_2\text{S}$  into  $\text{CuSO}_4$  and CuO. The roasted bricks are passed through rolls, leached and washed by a counter-current system with electrolyte containing 7 per cent.  $\text{H}_2\text{SO}_4$ , and with  $\text{H}_2\text{O}$ . The resulting copper liquor contains 5 per cent. Cu and 1 per cent. free  $\text{SO}_3$ ; it is cleared in a filter-press and run into a storage vat to be drawn into four electrolyzing tanks. These have a capacity of 35 cu. ft., are of wood and lead-lined, hold nine covered lead-plate anodes and eight copper stripping-plate cathodes ( $\frac{1}{3}\frac{1}{2}$  in.). The electrolyte is stirred by means of vertical wooden slats attached to wooden arms receiving a reciprocating motion through an eccentric. A current of 900 amp. at from 2.25 to 2.50 volt. passes through the four vats; the density is 9.3 amp. per square foot cathode area. Copper is deposited at the rate of 1.1 g. per ampere hour, which is equal to 1 lb. Cu in 0.90 kw.-hr. and corresponds to a power consumption of 3.5 h.p.-hr. The plant with its four vats, producing 220 lb. Cu per day, has a dynamo furnishing a current of 900 amp. at 10 volt. In 35 hr. the Cu-content of the electrolyte is reduced to 1-1.5 per cent., and the free  $\text{SO}_3$  increased to 7 per cent.; the liquor is withdrawn from the vats to serve again as solvent, and the vats receive a new charge from the storage tank. In one month the cathode deposits have attained a thickness of 1.00-1.25 in. when they are replaced by starting-sheets and are sold without casting.

At Karkarlinsk, the copper mineral is oxide, the ore assays 5 per cent. Cu, the copper solution contains 2.5 per cent. Cu, and the electrolyzed solution 0.5 per cent. Cu.

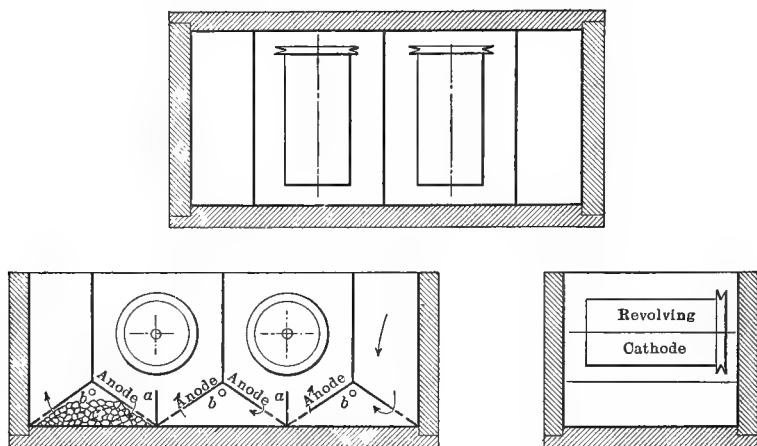
**206. The Carmichael Process.**<sup>1</sup>—In this process oxide or roasted sulphide copper ore is treated with hot dilute  $\text{H}_2\text{SO}_4$ ; the copper liquor is electrolyzed with insoluble lead anodes in the presence of  $\text{SO}_2$  which acts as a depolarizer, furnishes fresh  $\text{H}_2\text{SO}_4$ , and stirs the electrolyte. At the Intercolonial plant of Dorchester, N. B., the  $\text{CuSO}_4$ -solution with Cu 2.5 per cent. and considerable free  $\text{H}_2\text{SO}_4$ , was impregnated with  $\text{SO}_2$ -gas, and electrolyzed in tanks arranged in cascades while  $\text{SO}_2$  was blown through the electrolyte. The electrodes were 1.5 in. apart, the current density was 6 amp. per square foot, the electromotive force of a tank 1.5 volt., the current efficiency 90 per cent.

<sup>1</sup> Johnson, *Electrochem. Ind.*, 1903, 1, 274.

Reinartz, *Metallurgie*, 1908, v, 202.

Austin, *Min. Meth.*, 1911, 11, 281.

The process has been recently investigated by Reinartz. The apparatus used is shown in Figs. 429-431. A wooden lead-lined vat is divided by sheet-lead plates into four compartments having hopper-shaped bottoms. The electrolyte entering the compartment to the right passes through the other three as indicated by the arrows and is made to flow in the prescribed path by baffle plates. The hopper-shaped bottom forms the anode, two revolving copper cylinders the cathode; the electrode—distance is 3 in.; the other partition plates are coated with acid-proof paint. In charging the vat, no electrolyte will reach the three gables of the bottom, as they are filled with air under a pressure corresponding to the depth of the liquor. Each gable space has an inlet-pipe for sulphurous gas, made up of 5 vol.  $\text{SO}_2$  and 95 vol. air, which is introduced



FIGS. 429-431.—Reinartz-Carmichael experimental electro-depositing, vat.

with suitable pressure under the left gable, and travels through a connecting pipe into the second and third gable-space, whence it passes off into the open. Thus the electrolyte is brought in contact with the gas. In order to increase the contact surface, the gable space to the left is filled with pyritic ore. In the first experiment, Table 102, pyritic ore was placed also on the hopper-shaped bottoms beneath the cathodes that it might act as a diaphragm; later it was removed. Tables 102, 103, and 104 give the results of the work.

Comparing Tables 102 and 103 with and without diaphragm, it is seen that in the absence of a diaphragm the voltage is reduced 30 per cent. while maintaining the same cathode current efficiency of about 95 per cent. and an anode efficiency of 65 per cent. In Table 104 no  $\text{SO}_2$  was passed through the electrolyte with experiments Nos. 1 and 2. The electrolyte was, however, already saturated with the gas; hence the current efficiency with experiment No. 1 attained the comparatively high figure of 70 per cent. and the ferric iron rose from 0.12 to 0.36 per cent. With the second experiment, the current efficiency fell to 26 per cent; in the third when gas was admitted it rose to 90 per cent.; of the 0.36 per cent. ferric sulphate 0.15 per cent. was reduced by the  $\text{SO}_2$ . The results

TABLE 102.—EXPERIMENTS, USING PYRITE DIAPHRAGM

No. of experiment	Amount of solution, liters	Composition of the electrolyte					Mean current strength, amp.	Mean potential, volts	Length of experiment, hours	Copper deposited, grams	Sulphuric acid produced, per cent.	Cathode current efficiency, per cent.	Anode current efficiency, per cent.	Cost, cents per lb. copper deposited
		Copper, per cent.	Ferrous iron, per cent.	Ferric iron, per cent.	Free sulphuric acid, per cent.	Total sulphuric acid, per cent.								
1	55	4.94	1.25	0.12	0.95	10.77	5	3.21	24	126	0.25	95	65	2.774
2	55	4.77	1.25	0.12	1.45	11.02	5	2.91	24	130		98		2.438
3	55	4.42	1.25	0.12	2.08	11.27	5	2.71	24	143		100		2.062
4	55	4.20	1.25	0.12	2.82	11.52	5	2.61	24	136		100		2.094

TABLE 103.—EXPERIMENTS WITHOUT DIAPHRAGM

No. of experiment	Amount of solution, liters	Composition of the electrolyte					Mean current strength, amp.	Mean potential, volts	Length of experiment, hours	Copper deposited, grams	Sulphuric acid produced, per cent.	Cathode current efficiency, per cent.	Anode current efficiency, per cent.	Cost, cents per lb. copper deposited
		Copper, per cent.	Ferrous iron, per cent.	Ferric iron, per cent.	Free sulphuric acid, per cent.	Total sulphuric acid, per cent.								
1	55	3.97	1.25	0.12	3.40	11.70	5	2.06	24	122	0.25	91	65	1.838
2	55	3.67	1.25	0.12	4.11	12.02	5	2.04	12	60		90		1.850
3	55	3.57	1.25	0.12	4.50	12.15	5	1.98	24	120		90		1.799
4	55	3.35	1.25	0.12	5.22	12.65	5	2.00	24	131		100		1.660
5	55	3.07	1.25	0.12	5.90	12.90	5	1.93	24	133		100		1.590

show that of the O appearing at the anode, from 60 to 65 per cent. can be utilized in the oxidation of  $\text{SO}_2$ ; that a cathode efficiency of 95 per cent. can be obtained without the use of a diaphragm from a ferruginous copper sulphate solution, with the recovery of a high quality of copper. Experiments carried out with pure  $\text{CuSO}_4$  showed that the cathode efficiency remained about the same, while the anode efficiency was reduced 5 per cent.

TABLE 104.—EXPERIMENTS SHOWING EFFECT OF  $\text{SO}_2$ 

No. of experiment	Composition of electrolyte			Copper deposited, grams	Length of experiment, hours	Mean current strength, amps.	Mean potential, volts	Current efficiency, per cent.	Cost, cents per lb. copper deposited
	Copper, per cent.	Ferrous iron, per cent.	Ferric iron, per cent.						
1	2.83	1.25	0.12	91	24	5	2.00	70	2.393
2	2.60	1.01	0.36	36	24	5	2.00	26	6.054
3	2.54	1.16	0.21	75	15	5	1.90	90	1.720

To the original tables of Reinartz have been added costs, cents per pound Cu deposited as figured by Austin. Thus in Table 102, experiment No. 1, the average current was 5 amp. at 3.21 volt;  $5 \times 3.21 = 16.05$  watt; divided by 1000 gives 0.01605 kw. This deposited 126 g. = 4.44 oz. Cu in 24 hr., hence required  $0.01605 \times 24 = 0.3852$  kw.-hr., which is equivalent to 1.3872 kw., hr. for 1 lb. Cu. Taking the kilowatt-hour at 2 cents makes the cost of depositing 1 lb. Cu 2.774 cents as given in the table.

**207. The Neill and Van Arsdale Processes.**<sup>1</sup>—In this process  $\text{SO}_2$  generated by roasting metallic sulphide in a kiln is forced through a series of tanks holding a watery pulp of oxide ore in order to form and hold in solution  $\text{CuSO}_3$ ; this salt is unstable, and changes when in contact with  $\text{CuO}$  into  $(\text{Cu}_2\text{SO}_3 + \text{CuSO}_3) + \text{CuSO}_4$ . Upon heating the solution, from 66 to 75 per cent. of the Cu is precipitated as  $\text{Cu}_2\text{SO}_3 + \text{CuSO}_3$  with the formation of some  $\text{CuSO}_4$ . The remaining Cu has to be recovered by other means, *e.g.*, by precipitation with Fe. The process at Caconino, Ariz., was not successful for mechanical reasons, but tests at the works of the Montana Ore Purchasing Co., Butte, with ore roasted in MacDougall furnaces, gave a total yield of 90 per cent. Cu with a direct extraction of 64 per cent. as  $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3$ .

In the Van Arsdale process,  $\text{SO}_2$  is used as a reducing and precipitating agent. Oxide ore is leached with  $\text{H}_2\text{SO}_4$ ; the solution is saturated with  $\text{SO}_2$  when the reaction  $3\text{CuSO}_4 + 3\text{SO}_2 + 4\text{H}_2\text{O} = \text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 + 4\text{H}_2\text{SO}_4$  takes place. The solution placed in a closed vessel and heated to  $100^\circ \text{C}$ . liberates gas which generates a pressure of 30 lb. causing the reaction  $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 + 4\text{H}_2\text{SO}_4 =$

<sup>1</sup> Neill, Circular 1901, *Min. Rep.*, 1902, XLVI, 395, 464; *Eng. Min. J.*, 1908, LXXXV, 556; *Min. Meth.*, 1910, I, 389.

Jennings, *J. Can. Min. Inst.*, 1901, IV, 123; *Eng. Min. J.*, 1901, LXXI, 400; 1908, LXXXV, 152, 821; LXXXVI, 418 (Westly-Sörensen process).

Van Arsdale, *Eng. Min. J.*, 1903, LXXV, 853 (Van Arsdale process).

Gin, *Zt. Electrochemie*, 1903, IX, 857.

Burfeind *Min. Rep.*, 1902, XLVI, 206, 464.

Zwaluwenburg, *Min. Meth.*, 1910, I, 376.

Austin, *op. cit.*, 1911, II, 241.

$\text{Cu} + 2\text{CuSO}_4 + 2\text{H}_2\text{SO}_4 + 2\text{SO}_2 + 2\text{H}_2\text{O}$  to take place; 40–50 per cent. of the Cu falls out as metal from an original solution with 10 per cent. Cu. Releasing the pressure causes most of the  $\text{SO}_2$  to pass off, so that the regenerated solvent can be used again. According to Gin<sup>1</sup> the temperature has to be 180° C. and the pressure 142 lb. The process has not been tested on a large scale.

**208. Stadtberge Process.** LEACHING WITH  $\text{HCl}$ .<sup>2</sup>—With the change of the ore from oxide to sulphide, the process has been replaced at Stadtberge by the Doetsch process (§ 221).

Oxide ore with about 2 per cent. Cu, crushed to 1 in., used to be leached for 3 days with  $\text{HCl}$  of 12–13° Bé in vats holding 75 tons (depth of charge 3.3 ft.) until the acid was neutralized and thereby enriched to 19–20° Bé. From the liquor, the Ag with part of the Cu was precipitated with Fe, and, later on, the remainder of the Cu. The leached ore, moist with  $\text{HCl}$ , was piled in heaps and allowed to weather for 12–15 weeks; decomposition was assisted by wetting at intervals with mother liquor from the precipitating vats. In this way 75 per cent. of the Cu was recovered. The twice-leached ore was removed to the dump to undergo further alteration by weathering. The drainage from the dump was collected and treated with Fe. An additional 17 or 18 per cent. Cu was thus recovered, making the entire yield of Cu 92–93 per cent.

Other examples of leaching with  $\text{HCl}$  are that of Rochlitz,<sup>3</sup> and the tests of Stahl.<sup>4</sup>

**209. The Greenawalt Process.**<sup>5</sup>—Oxide or roasted sulphide copper ore is leached with  $\text{HCl}$  dissolved in brine; the  $\text{CuCl}_2$  formed is reduced to  $\text{Cu}_2\text{Cl}_2$  by  $\text{SO}_2$ -gas, viz.,  $2\text{CuCl}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = \text{Cu}_2\text{Cl}_2 + 2\text{HCl} + \text{H}_2\text{SO}_4$ , and some  $\text{HCl}$  formed by  $\text{H}_2\text{SO}_4 + 2\text{NaCl} = 2\text{HCl} + \text{Na}_2\text{SO}_4$ ; the solution of  $\text{Cu}_2\text{Cl}_2$  in  $\text{HCl}$  and  $\text{NaCl}$  is electrolyzed with Acheson graphite electrodes and at the same time  $\text{SO}_2$  pumped into the vat, whereby the Cl set free is converted into  $\text{HCl}$ , the reactions being  $\text{Cu}_2\text{Cl}_2 + \text{current} = \text{Cu}_2 + \text{Cl}_2$  and  $\text{Cl}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{HCl} + \text{H}_2\text{SO}_4$ , also  $\text{H}_2\text{SO}_4 + 2\text{NaCl} = 2\text{HCl} + \text{Na}_2\text{SO}_4$ . It is thus seen that the raw materials consumed are salt ( $\frac{1}{8}$  lb.  $\text{NaCl}$  for 1 lb. Cu), and  $\text{SO}_2$ . Impurities, such as Bi, As, and Sb, are to be precipitated by  $\text{H}_2\text{S}$  from decopperized liquor. Iron going into solution as  $\text{FeCl}_2$  is precipitated as  $\text{Fe}_2\text{O}_3$  by  $\text{CuO}$  according to the Hunt-Douglas reaction  $\text{FeCl}_2 + 3\text{CuO} = \text{Fe}_2\text{O}_3 + \text{CuCl}_2 + \text{Cu}_2\text{Cl}_2$ . For a complete elimination of base metal,  $\text{NaCl}$  is electrolyzed, giving Cl and  $\text{NaOH}$  (2 kw.-hr. furnishing 1 lb. Cl and 1.5 lb.  $\text{NaOH}$ ), the Cl is conducted with  $\text{SO}_2$  into brine:  $2\text{Cl} + \text{SO}_2 + 2\text{H}_2\text{O} + 2\text{NaCl} = 4\text{HCl} + \text{Na}_2\text{SO}_4$ , and the  $\text{NaOH}$  serves to precipi-

<sup>1</sup> V Internat. Congress Angewandte Chemie, 1903, II, 116.

<sup>2</sup> Miszke, *Oest. Zt. Berg. Hüttenw.*, 1871, XIX, 108.

Gerhardt, *Zt. Verein. deutsch. Ing.*, 1872, XVI, 305.

Francke, *Metallurgie*, 1910, VII, 484.

Mengler, *op. cit.*, 1911, VIII, 176.

<sup>3</sup> Meyer, *Berg. Hüttenm. Z.*, 1862, XXI, 173, 201.

<sup>4</sup> *Op. cit.*, 1894, LIII, 65.

<sup>5</sup> Greenawalt, *Eng. Min. J.*, 1910, XC, 1064; Austin, *Min. Meth.*, 1911, II, 339; Greenawalt, "Hydrometallurgy of Copper," 1912, p. 349.

tate the base metals. Accumulation of  $\text{Na}_2\text{SO}_4$  is said to have no deleterious effect.

At the experimental plant in Denver, Colo., with a variation in current density of 6.2 to 66 amp. per square foot cathode area, 1 lb. Cu was deposited per kilowatt-hour. On a basis of \$50 per kilowatt year and 1 lb. Cu per kilowatt-hour the cost of electro-deposition of 1 lb. Cu is estimated to be 5.8 cents. The cost of a 100-ton plant for 5-per cent. Cu ore is given as \$120,000 to which, with sulphide ore, \$30,000 should be added for a roasting plant. The cost of treatment per ton oxide ore is estimated at \$1.96, and \$2.71 per ton sulphide ore, if \$0.75 is the cost of roasting.

**210. Leaching Atacamite.**—This chloride mineral cannot be smelted direct, as about 50 per cent. of the Cu is lost by volatilization, hence wet processes have to be used. According to Argandoña,<sup>1</sup> heating the ore in a cast-iron retort to 230° C. and conducting over it steam at 2 lb. pressure decomposes the mineral:  $\text{CuCl}_2 + \text{H}_2\text{O} = \text{CuO} + 2\text{HCl}$ . The CuO is smelted and low-grade ore leached with the condensed HCl.

Evans<sup>2</sup> proposes solution with HCl and precipitation with  $\text{H}_2\text{S}$ .

Thompson-McGovern<sup>3</sup> discuss the leaching and electro-deposition with an anode of fused magnetite, in Chile, of bronchantite,  $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ , associated with the NaCl and  $\text{NaNO}_3$  in a siliceous decomposed granite.<sup>4</sup>

**211. Leaching Sulphide Ore after Conversion into Sulphate by Weathering.** Pyritic ore which is readily disintegrated by atmospheric agencies, such as free-burning pyrite and especially marcasite, and which carries disseminated copper mineral readily sulphatized, such as chalcocite, is suited for weathering; covellite is slowly sulphatized, and chalcopyrite hardly at all, unless it is first converted into chalcocite,<sup>5</sup> which is a very slow process. But even under the most favorable conditions the process is lengthy, requiring years for a satisfactory extraction. The pyritic material while disintegrated in the process is only slightly altered and can be utilized for the production of  $\text{SO}_2$  in the manufacture of  $\text{H}_2\text{SO}_4$ .

The leading chemical reactions taking place in weathering have been variously formulated.<sup>6</sup> The simplest is that of Jones:  $\text{FeS}_2 + 7\text{O} + \text{H}_2\text{O} = \text{FeSO}_4 + \text{H}_2\text{SO}_4$ ;  $2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{O} = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$ ;  $\text{Fe}_2(\text{SO}_4)_3 + \text{Cu}_2\text{S} = 2\text{FeSO}_4 + \text{CuSO}_4 + \text{CuS}$ ;  $\text{Fe}_2(\text{SO}_4)_3 + \text{CuS} + \text{H}_2\text{O} + 3\text{O} = 2\text{FeSO}_4 + \text{CuSO}_4 + \text{H}_2\text{SO}_4$ . The  $\text{H}_2\text{SO}_4$  set free would further decompose  $\text{Cu}_2\text{S}$  and  $\text{CuS}$ . Winchell suggests that inasmuch as  $\text{Cu}_2\text{S}$  is more readily oxidized than  $\text{FeS}_2$ , its solution may precede that of  $\text{FeS}_2$  and hasten the oxidation of the latter. The sulphate

<sup>1</sup> *Min. J.*, 1906, LXXIX, 854; *Eng. Min. J.*, 1906, LXXXII, 205.

<sup>2</sup> *Min. J.*, 1908, LXXXIV, 453.

<sup>3</sup> *Eng. Min. J.*, 1913, XCV, 171.

<sup>4</sup> See also: Editor, *Min. Sc. Press*, 1913, CVI, 933.

<sup>5</sup> Finlayson, *Tr. Inst. Min. Met.*, 1910-11, XX, 70.

<sup>6</sup> Emmens, *Eng. Min. J.*, 1892, LIV, 582.

Probert, *Econ. Geol.*, 1903, LXXVI, 958.

Stokes, *op. cit.*, 1907, II, 14, 290 (Winchell).

Jones, *Tr. A. I. M. E.*, 1905, XXXV, 3.

tization of  $\text{CuS}_x$  is accompanied by the conversion of sulphides of Ni, Pb and Zn into sulphates and the oxidation and solution of As, Sb, and Bi. From the solution Fe will precipitate Cu first and later on part of the As, Sb, and Bi. Table 105 gives some data by Gibbs<sup>1</sup> upon the elimination of these three elements.

TABLE 105.—ELIMINATION OF AS, SB AND BI BY WEATHERING

Metal	Pyrite		Precipitate		Total elimination %
	% actual	% relative, Cu=100	% actual	% relative Cu=100	
Cu.....	2.00	100.0	62.0	100.0	.....
As.....	0.40	20.0	3.5	5.64	71.8
Sb.....	0.030	1.5	0.08	0.129	91.4
Bi.....	0.016	0.8	0.06	0.097	87.9

**212. Leaching at Rio Tinto.**—The leading example is that of Rio Tinto, Spain,<sup>2</sup> where weathering has superseded all other processes, especially since heap-roasting has been forbidden since 1888. At San Domingo, Portugal, the law went into effect in 1878. The ore is a massive pyrite (marcasite) and an impregnated schist with from 1 to 3, average 2.5 per cent. Cu, and 45-48 per cent. S. The analyses<sup>3</sup> given in Table 106 show the general character of the ores exported and treated locally. Other analyses are published by Vogt.<sup>4</sup>

TABLE 106.—ORE OF RIO TINTO, SPAIN

Ores	Massive pyrite		Schistose pyrite
	Export ore	Local treatment ore	Local treatment ore
Fe.....	43.1	42.8	0.10
S.....	49.5	48.3	0.15
Cu.....	2.5-3.0	1.5-2.0	1.0-1.25
Pb.....	0.3	1.3	....
Zn.....	0.8	1.8	0.05
As.....	0.4	0.7	....
H <sub>2</sub> O.....	0.5	0.8	3.15
SiO <sub>2</sub> .....	0.6	0.7	93.6
O and various metals..	1.2	1.1	....
Total.....	99.4	99.5	98.3

<sup>1</sup> *Tr. A. I. M. E.*, 1903, XXXIII, 667.

<sup>2</sup> Deumié, *Bull. Soc. Ind. Min.*, 1887, I, 843; Launay, *Ann. Min.*, 1889, XVI, 491; *Berg. Hüttenm. Z.*, 1890, XLIX, 229, with cross ref.; *Eng. Min. J.*, 1890, L, 741; Brown, *J. Soc. Chem. Ind.*, 1894, XIII, 472; *Dingl. Polyt. J.*, 1894, CCXCIV, 48; *Berg. Hüttenm. Z.*, 1895, LIV, 8; Courtney, *Proc. Inst. Civ. Eng.*, 1896, CXXV, 136; Adcock, *Min. Ind.*, 1900, IX, 235; Chalon, *Rev. Un. Min.*, 1902, LVII, 205; Jones, *Tr. A. I. M. E.*, 1905, XXXV, 3; Truchot, *Sixth Internat. Congress Appl. Chem.*, 1906, II, 170; *Bull. Soc. Ind. Min.*, 1908, IX, 68; *Min. Ind.*, 1906, XV, 288, his treatise, p. 163; Probert, *Min. Sc. Press*, 1908, XCVI, 27; Corresp., *Eng. Min. J.*, 1910, LXXXIX, 748.

<sup>3</sup> *Eng. Min. J.*, 1907, LXXIX, 371.

<sup>4</sup> *Zt. prakt. Geologie*, 1894, II, 44; *Zt. Berg. Hütten. Salin. Wesen. i. P.*, 1898, XLVI, 225.

The ore is crushed to pass a 3-in. ring and sorted into coarse and fine in the ratio of 4:5 with 1.25 and 2.25 per cent. Cu. The site for a weathering heap is a slightly sloping ground. On this, stone flues are erected, each 12 in. in diameter, to serve as air-inlets and draining-channels; on the junctions of the flues are erected, as the heap is being formed, chimneys 80 ft. apart, also of rough stone. The heap is now formed of alternate layers of coarse and fine ore, the start being made with side-dump cars on the upper part of the site. The top layer consists of fines in order to assist in the distribution of water. The heap, which has a horizontal surface, is 33-40 ft. high and holds 100,000 tons of ore. On the surface are formed squares separated by ridges to regulate the flow of water admitted through gutters. While the heap is being formed,  $H_2O$  is admitted to dissolve existing  $CuSO_4$  and to furnish the ore the moisture necessary for oxidation. The temperature in the chimneys may rise to 82 and 90° C. and even to the kindling temperature of the ore; it is, however, not allowed to exceed 82° C.; at some mines it is held at 30-32° C., and the average temperature is 45-60° C. If the heat rises too quickly in places, the chimneys are closed, which not only checks such rise, but causes the oxidation to spread more evenly through the heap. The combined warmth and oxidation cause hardly—perceptible fissures to form in the pyritic ore into which solvents penetrate, dissolve the Cu, and more or less disintegrate the disulphide. When oxidation has proceeded sufficiently,  $H_2O$  charged with liquor from the cementation tanks is run on at the rate of 50 cu. m. (13,210 gal.) per hour until the soluble Cu has been extracted. The water is turned off, the heap allowed to drain, and the sulphide mineral to oxidize, whereupon leaching is repeated. After about one year, the surface is dressed, *i.e.*, the locations of the squares and ridges are interchanged, and the gutters correspondingly shifted; further, the edge of the heap, having become hardened by crystallized copper salt, is dug into and formed into terraces in order that the salts may be readily extracted. It takes from six to seven years with massive ore, and from three to four years with schistose ore to reduce the Cu-content to 0.25-0.30 per cent., which is as far as the extraction can be carried with a profit. There is a loss of 15 to 30 per cent. of weight of the ore in the process. The exhausted ore (washed sulphur ore) is removed and shipped to sulphuric acid plants. Upon screening through a 2-mesh sieve to prepare for the coarse- and fine-ore roasting kilns, as much as 50 per cent. will pass through the sieve, showing how strongly it becomes disintegrated by weathering.

The solution with from 0.015 to 0.5 and even 0.6 per cent. Cu is of a reddish-green color; it contains  $Fe_2.(SO_4)_3$ ,  $FeSO_4$ ,  $CuSO_4$ ,  $H_2SO_4$ , besides  $Bi_2.(SO_4)_3$ ,  $Sb_2.(SO_4)_3$ ,  $Ag_2SO_4$ , and  $Fe_2.(AsO_4)_2$ . In order to reduce the Fe-consuming  $Fe_2.(SO_4)_3$  to  $FeSO_4$ , the liquor from the heap is run over freshly mined pyrite-fines when the reaction  $7Fe_2.(SO_4)_3 + FeS_2 + 8H_2O = 15FeSO_4 + 8H_2SO_4$  takes place.

The "filter-bed" is laid in a reservoir formed by a masonry dam across a small ravine having a slope of about 5°; its surface is topped with the finest material and divided into 50-ft. squares. The liquor remains in contact with



the filter until its color has changed to a clear blue, when 90 per cent. of the  $\text{Fe}_2(\text{SO}_4)_3$  has been reduced to  $\text{FeSO}_4$ . It contains per cubic meter (35.31 cu. ft.) 4 kg. (8.8 lb.) Cu, 1 (2.2 lb.)  $\text{Fe}_2\text{O}_3$ , 20 (44 lb.) FeO, 10 (22 lb.)  $\text{H}_2\text{SO}_4$  and 0.3 (0.66 lb.) As.

The precipitation (cementation) with pig iron is carried on in a series of flumes placed along the slope of a hill so that the liquor flows to and fro until after passing through a mile of flume it is discharged and collected in part to be used again as solvent. Each main flume is made of 2, 3, or 4 smaller flumes separated from one another by walls. Each flume is 320 ft. long, 5.5 ft. wide and 2.25 ft. deep, constructed of 9×3 in. planks held together by wooden frames set in cement, the joints of the planks being rope-calked and painted with asphalt. In order to permit cutting out of circuit, each end of a flume is provided with a door with holes, closed by plugs, to drain off the liquor before removing the cement Cu. The fall of the flumes increases from inlet to outlet, *i. e.*, 0.5 per cent. for the first third, 1 per cent. for the second, and 2 per cent. for the last third, in order to diminish the increased Fe-consumption by the partly decopperized liquor. The bottom of a flume is loosely covered with boards, and the pig iron piled in grids at right angles to one another until the flume is filled, 1 ft. of flume holding 1 ton of pig iron. The liquor from the filter bed passes into a reservoir and thence runs into the flumes at the rate of 300 cu. m. (10,595 cu. ft. or 79,260 gal.) per hour. In summer it reaches a temperature of 38° C., the higher the temperature the more rapid the precipitation. The precipitate near the head of the flume is the purest (Cu 93-94, As < 0.3 per cent.) and adheres to the pig iron; lower down it is still red but becomes granular (Cu 75-90, As 0.5 per cent.); the remainder is more or less black (Cu 50, As 5 per cent.) and contains most of the graphite. Some flumes are cleaned daily; the liquor is run into settling tanks to recover suspended Cu, the pig iron is removed and piled on the dividing wall, adhering Cu knocked off, and the iron then returned to the flume. The cement Cu goes to a cleaning and concentrating plant. Here red precipitate (Cu 70 per cent.) is screened, washed with a hose, compressed into cylinders, dried, and shipped. Black precipitate is briquetted and sun-dried, and so hardens and is ready to go to the blast-furnaces. The liquor with Cu 15-20 g. per cubic meter goes to waste, as the Fe-consumption is too high to pay for the recovery of the Cu. The extraction of Cu reaches 95 per cent. Table 107 gives analyses of in- and out-going liquors.

TABLE 107.—HEAD- AND TAIL-LIQUORS OF RIO TINTO

Liquor	Per cent.					Spec. gr.
	Cu	FeO	$\text{Fe}_2\text{O}_3$	$\text{H}_2\text{SO}_4$	Tot. solids	
Head.....	0.2715	1.3908	0.0610	0.4874	7.0872	1.05818
Tail.....	0.0019	1.7202	.....	0.4129	6.9662	1.05718

The consumption of iron under favorable circumstances is 1.3-1.5 tons of pig iron (with 92 per cent. Fe) for 1 ton of Cu; usually it is nearer 1.75-2 tons.

In view of the fact that the prices paid for pyrite have been increasing, be-

cause of the great advances made in the extraction of the Cu by the Longmaid-Henderson process (§ 225) and the briquetting and sintering of the leached iron oxide,<sup>1</sup> it is probable that the weathering process will be abandoned and the ore sold direct to the acid-maker.

**213. Leaching Ore in Place.**—This has been tried at Schmoellnitz, Hungary, by Buddeus;<sup>2</sup> in England, and at Chase Creek Canyon, Ariz., by Austin.<sup>3</sup> The mines of Schmoellnitz drowned in 1878 were pumped out in 1904, when the Cu recovered from the mine-water paid for the pumping. Durant<sup>4</sup> records the flooding of a mine in England from two to four times a year, recovering first Cu from the water and later iron ochre, after which the water is used again for filling the mine.

At Chase Creek Canyon, Austin experimented with the leaching of disseminated sulphide copper ore in place, by opening the ore-body in several horizons 50 ft. apart with drifts and cross-cuts, and introducing water which, filtering through the intervening rock, dissolved the Cu. The solutions were collected in a shaft starting from the lowest level, placed below the natural drainage of the locality, and then pumped into precipitating tanks. It was found that 1 ton of solution contained 0.4 lb. Cu, but there was not enough of it. Adverse conditions necessitated the abandoning of experiments to increase the amount.

**214. Leaching Sulphide Ore after Conversion into Sulphate by Sulphatizing Roasting.**<sup>5</sup>—The ore to be suited for this process must be a cupriferous pyrite, rich in  $\text{FeS}_2$ , poor in  $\text{CuS}_2$ ; if there is not enough  $\text{FeS}_2$ , this will have to be supplied; sulphatizing agents such as  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{NaHSO}_4$  have been added to the ore-charge.

The roast has to be carried on slowly and at a low temperature. The ore may be in lump-form or finely divided. Lump ore is roasted in heaps or kilns, fine ore in kilns or muffle-furnaces. Lump ore roasted in heaps will always be imperfectly sulphatized. A satisfactory yield in Cu can be obtained only by supplementing the roasting by some additional process such as weathering; the same is likely to be true with kiln-roasted ore whether this is coarse or fine; fine-ore muffle-furnaces which permit a good control of temperature and air give a good extraction without necessitating any auxiliary treatment.

**215. Sulphatizing Heap Roasts.**—1. *Rio Tinto*<sup>6</sup> is the best-known example where the process of heap roasting was carried on, until 1888 when the passing-

<sup>1</sup> Hofman, "General Metallurgy," 1913, p. 628 and foll.

<sup>2</sup> *Berg. Hüttenm. Z.*, 1904, LXIII, 13, 41, 73.

<sup>3</sup> *Min. Melh.*, 1911, II, 153, 187; *Comments Eng. Min. J.*, 1911, XCXI, Channing, 601; Henry, 699; Webber, 700; Webber 1911, XCII, 197.

<sup>4</sup> *Eng. Min. J.*, 1911, XCII, 928.

<sup>5</sup> Experiments of Schoeller on Slimes, *J. Soc. Chem. Ind.*, 1913, XXXII, 677.

<sup>6</sup> Deumié, *Bull. Soc. Ind. Min.*, 1887, I, 835.

Launay, *Ann. Min.*, 1889, XVI, 491; *Berg. Hüttenm. Z.*, 1890, XLIX, 229; *Eng. Min. J.*, 1890, I, 741.

Collins, *Tr. Inst. Min. Met.*, 1893-94, II, 17.

Courtney, *Proc. Inst. Civ. Eng.*, 1895-96, CXXV, 135.

Chalon, *Rev. Un. Min.*, 1902, LVII, 201.

Correspondent, *Min. J.*, 1910, LXXXIX, 731.

off of the sulphurous gases into the air was forbidden by law. Along the floor on which a heap is to be erected are built horizontal dry-stone air-flues 12-15 in. wide  $\times$  15-18 in. high. Usually three flues run longitudinally, 13 ft. apart, and one transversely. At the intersections dry-stone chimneys are erected. Small heaps, 20-26 ft. in diam. and 10 ft. high, hold 200 tons of ore, burn two months, and require 0.21 cord of wood per ton of ore; large heaps are oblong, 56 $\times$ 33 ft., and 11-12 ft. high, hold 1500 tons of ore, burn six months, and require only 0.07 cord; medium-size heaps, 98 $\times$ 16 ft. and 8 ft. high, hold 330 tons of ore. The loss in weight by roasting is about 12 per cent. Small heaps yield more  $\text{CuSO}_4$  than large. The average extraction of Cu is 84 per cent. Roasted ore is transferred in 2-ton side-dump cars to cemented and asphalted masonry vats, 30 ft. long by 8 ft. wide by 3 ft. deep, having false bottoms of rough planks; and is leached with water in five to seven consecutive washings of 36 cu. ft. of water per ton of ore, each lasting 24 hr. The later practice was to wash the ore in place as in the weathering process, and thus save handling.

TABLE 108.—SULPHATIZING ROASTING AND LEACHING AT RIO TINTO IN 1892

	Raw ore	Roasted ore	Leached ore
S.....	48.0	6.7	7.5
Fe.....	41.0	39.0	55.0
Cu.....	2.2	2.4	1.0
Pb.....	2.3	2.8	3.0
Zn.....	1.5	1.6	1.0
As.....	1.0	0.5	0.2
H <sub>2</sub> O.....	0.2	13.0	4.5
O, Loss.....	1.3	31.0	25.3
Insoluble.....	2.5	3.0	2.5
Total.....	100.0	100.0	100.0

The brown copper liquor with 120-225 g. Cu per gallon is collected in a reservoir filled with raw fines as in the weathering process (§ 212) to reduce  $\text{Fe}_2(\text{SO}_4)_3$  to  $\text{FeSO}_4$ , drawn into precipitating vats, 8 ft. wide by 3 ft. deep, charged with Fe, and then through precipitating flumes, 3-6 ft. wide, 1.5 ft. deep and over 1 mile long with a fall increasing from 0.4 to 2 per cent. The iron consumption is 1.25 Fe:1 Cu. The cement copper with 80 per cent. Cu is dried, packed, and shipped. The leached ore retains 0.20 per cent. Cu; it is piled in waste heaps holding as much as 50,000 tons, weathered, and leached at intervals. The roasted ore weathers very slowly. In order to hasten decomposition, small heaps of raw ore are built against the large pile, ignited, and the fumes are made to enter the pile as much as possible.

The elimination of As, Sb, and Bi by roasting is, according to Gibb,<sup>1</sup> As 76.8, Sb 22.0, Bi 14.8 per cent.

2. COPPEROPOLIS, CAL.<sup>2</sup>—Slaty pyritic ore with chalcopyrite containing

<sup>1</sup> *Tr. A. I. M. E.*, 1903, XXXIII, 668.

<sup>2</sup> *Bull. No. 23, State Mineralogist Cal.*, 1902, p. 193; Private Communications by F. H. Harvey, 1893, 1911, and G. McM. Ross, 1912; process abandoned in 1904.

5-5.5 per cent. Cu is crushed to pass a 3.5-in. ring, piled on two layers of cord wood, placed crosswise and covered with brushwood, to form heaps 8-16 ft. wide and 4-12 ft. high, holding 3000 tons and roasting four months. The roasted ore, in which 40 per cent. of the Cu is present as  $\text{CuSO}_4$ , is transferred to inclined wooden floors covered with tar paper, piled in heaps 300 by 150 by 15 ft., covered with undecomposed fines of the roast heap, and leached with  $\text{H}_2\text{O}$  and mother liquor from the precipitating vats. The solution with 7 per cent. Cu, some  $\text{FeO}$ ,  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$ , is run into two cement storage vats 14 by 14 by 16 ft. and thence drawn into a wooden copper-lined horizontal precipitating barrel 30 by 5 ft. supported by trunnions and provided with two charging openings and one relief valve for the escape of  $\text{H}$ . The barrel holds 3000 gal. of liquor, is charged with iron, rotated at a speed of 4 r.p. hr., and precipitates the Cu in 2 hr. The decopperized solution and cement Cu are discharged through a coarse screen, attached to the charging opening, to retain the iron in the barrel, and through a second screen, to retain coarse particles, into one of two settling tanks; the clear mother liquor is drawn off to be used as a solvent. The cement copper, 90-97 per cent. Cu, is washed, transferred to a drainage floor, dried on cast-iron pans heated by a direct fire from cord wood, and shipped. The fines covering the roasted heap are removed and placed on the wood bed of another heap or beneath it, as they form a layer that reduces loss of solution into the ground. The yield of copper is 40 per cent., the iron consumption is 1.15 Fe : 1 Cu.

3. AGORDO, ITALY.<sup>1</sup>—The distinguishing feature of the operation formerly carried out here is kernel roasting (§ 54) of pyritic ore with Cu 1.60, Fe 42.00, S 20.00, As 1.40, Insol. 5.00 per cent., which gives 13 per cent. kernels with 3-6 per cent. Cu to be smelted, and 87 per cent. rinds with < 0.5 per cent. Cu to be leached. There are 64 vats of 1400 to 1700 cu. ft. capacity. A tank is filled in part with liquor of 14-15° Bé, then charged with about 4 tons of ore, which remains in contact with the liquor for 24 hr. The solution, now of 31-34° Bé, is drawn off, clarified, the  $\text{Fe}_2(\text{SO}_4)_3$  reduced by  $\text{SO}_2$  gas to  $\text{FeSO}_4$ , run into vats, 13 ft. 1.5 in. long by 9 ft. 10 in. wide by 4 ft. 11 in. deep, and the Cu precipitated by Fe; the  $\text{FeSO}_4$  formed is recovered as green vitriol. The leached ore is washed twice, the  $\text{H}_2\text{O}$  remaining 24 hr. in contact in each wash. With an unsatisfactory extraction, the leached ore is spread as a cover over a roast heap and then leached again. When the Cu-content has been reduced to 0.25 per cent., the ore goes to the dump. This represents an extraction of only 50 per cent. The consumption of iron is 2.5 Fe : 1 Cu; the high figure is due to the  $\text{H}_2\text{SO}_4$  formed by the reduction of  $\text{Fe}_2(\text{SO}_4)_3$  with  $\text{SO}_2$ ; without this reduction the iron consumption was 3.27 Fe : 1 Cu.

4. OTHER LOCALITIES.—Kernel roasting followed by leaching was tried at Ducktown, Tenn.<sup>2</sup> Other older examples are: Balan, Transylvania;<sup>3</sup>

<sup>1</sup>Mazzuoli, *Ann. Min.*, 1876, IX, 1900; *Berg. Hüttenm. Z.*, 1876, XXXV, 363.

Egleston, *School Mines Quart.*, 1887-88, IX, 124, 256.

Ernst-Monaco, *Berg. Hüttenm. Z.*, 1891, I, 26.

<sup>2</sup>Wendt, *School Mines Quart.*, 1885-86, VII, 218.

<sup>3</sup>Flechner, *Oest. Zt. Berg. Hüttenw.*, 1882, XXX, 355; 1883, XXXI, 455, 463.

Maidenpec, Servia;<sup>1</sup> Szalathna, Hungary;<sup>2</sup> Colorado<sup>3</sup> (*Monier* process); Terrino process (Heating with  $\text{Fe}_2(\text{NO}_3)_6$ ).<sup>4</sup>

All the sulphatizing roasting processes enumerated suffer from the drawback that there is an imperfect control of temperature and air, with the consequence that the ore is roasted either too little or too much, and in most cases is more or less sintered. The imperfect extraction of Cu in the first leaching requires additional treatment of the ore in order to increase the yield.

**216. Sulphatizing Muffle Roasts.**—Roasting pyritic concentrate in a muffle furnace under controlled temperature and air has been carried out first in the laboratory by Warlimont,<sup>5</sup> and then at the works of Predazzo, Italy, by Hesse.<sup>6</sup>

Other laboratory data are those of Hollis-Lannon-Quayle-Grommon,<sup>7</sup> Austin,<sup>8</sup> Handy.<sup>9</sup> Large scale work has been carried on by Wedge in his multiple-hearth down-draft muffle furnace, Figs. 446-447, and Laist.<sup>10</sup> The results of Wedge are assembled in Table 109; the work of Laist is discussed in § 219.

At the works of Predazzo, Italy,<sup>11</sup> is treated a 60-mesh concentrate in which the Cu occurs as chalcopyrite; it contains Cu 7.1, Fe 17.25, S 8.66, CaO 2.90, MgO 0.10,  $\text{P}_2\text{O}_5$  0.23,  $\text{Al}_2\text{O}_3$  5.45, Insol. 49.97 per cent. The roasting furnace is a horizontal boiler-iron revolving

TABLE 109.—SULPHATIZING ROASTS IN THE WEDGE MULTIPLE-HEARTH DOWN-DRAFT MUFFLE FURNACE

Copper-bearing mineral	Analysis raw ore, per cent.					Kiln-roasting gave extraction, per cent.					Muffle-roasting gave extraction, per cent.				
	Cu	Fe	S	$\text{SiO}_2$ (Insol.)	CaO	MgO	$\text{Al}_2\text{O}_3$	In water	In acid	In soluble	Total soluble	S in kiln-roasted ore, per cent.	In water	In acid	In soluble
Chalcopyrite.....	1.07	49.25	32.60	6.80	.....	2.18	1.59	27.8	63.4	8.8	91.2	4.7	60.3	38.1	1.6
Chalcopyrite.....	3.52	9.76	9.54	66.5	.....	.....	.....	.....	.....	.....	.....	.....	60.70	20.22	20.8
Chalcopyrite.....	4.38	9.61	16.37	61.21	1.10	0.72	.....	.....	.....	.....	.....	.....	73.7	15.7	10.6
Bornite, some silicate and carbonate.	3.40	11.05	13.02	63.90	.....	.....	.....	.....	.....	.....	.....	.....	80.80	11.8	7.4
Oxide.....	3.14	2.25	none <sup>1</sup>	85.5	.....	.....	.....	.....	.....	.....	.....	.....	92.0	.....	.....
Silicate.....	1.86	2.79	0.80 <sup>2</sup>	88.3	.....	3.4 <sup>3</sup>	2.58	.....	.....	.....	.....	.....	95.2	.....	.....

<sup>3</sup> Figure is  $\text{H}_2\text{O}$ .

<sup>2</sup> Six per cent. pyrite (4.70 per cent. S) added.

<sup>1</sup> Five per cent. pyrite (47.5 per cent. S) added.

<sup>1</sup> Simons, *Berg. Hüttenm. Z.*, 1885, XLIV, 58.

<sup>2</sup> Beaugay, *Ann. Min.*, 1884, VI, 453, *Berg. Hüttenm. Z.*, 1885, XLIV, 242.

Farbaky, *op. cit.*, 1894, LIII, 175, 183, 225, 241, 249.

<sup>3</sup> Reichenecker, *op. cit.*, 1870, XXIX, 449.

Trippel, *Eng. Min. J.*, 1872, XIV, 114, 129.

<sup>4</sup> *Berg. Hüttenm. Z.*, 1888, XLVII, 171.

<sup>5</sup> *Metallurgie*, 1909, VI, 83, 127.

<sup>6</sup> *Op. cit.*, 1909, VI, 580.

<sup>7</sup> *Colo. School Mines Bull.*, 1908, IV, 112.

<sup>8</sup> *Mines and Meth.*, 1912, IV, 9.

<sup>9</sup> *Eng. Min. J.*, 1912, XCIV, 487.

<sup>10</sup> *Eighth Internat. Congr. Appl. Chem.*, New York, 1912, III, 151; *Tr. A. I. M. E.* 1913, XLIV, 818, *Op. cit.* 1913, XLVI, 362.

<sup>11</sup> Hesse, *Metallurgie*, 1909, VI, 580, with drawings.

cylinder, 6 ft.  $6\frac{3}{4}$  in. in diameter and 12 ft.  $5\frac{1}{2}$  in. long, resembling a Brückner cylinder, provided with ribs to raise and stir the ore. The cylinder is enclosed in a brick chamber and heated externally from three naphtha atomizing burners, 6 ft.  $6\frac{3}{4}$  in. from the shell; the flames strike a bridge wall which deflects the gases downward that they may pass around the cylinder and leave near the top through a flue provided with a damper. The furnace makes 0.75 r.p.m., and receives a charge of 3 tons which it roasts in 13-14 hr.; discharging and recharging take 4-5 hr., thus making the capacity for 24 hr. 4-5 tons; one man per shift tends the furnace. Through the air-inlet collar is inserted an iron-constantan thermo-electric pyrometer to measure the temperature, which at first is held at  $480^{\circ}$  C. and later at  $560^{\circ}$ . The outlet collar is connected with an earthenware acid-proof suction fan which draws in the air necessary for oxidation (an occasional lack of air may be supplemented by an auxiliary fan blower) and delivers the gases to a dust flue connected with a stack. Of the Cu, 65 per cent. is water-soluble, 31 per cent. acid-soluble (hot  $\text{H}_2\text{SO}_4$  of  $17^{\circ}$  Bé.). With ore containing 20 per cent. Cu, 98 per cent. is soluble in acid. The brick lining of the furnace becomes incrustated in time; the crust has to be removed several times a year, but 80 per cent. of its Cu is water-soluble, and an additional 14-16 per cent. acid-soluble. The furnace makes 20 per cent. flue-dust; 93 per cent. of its Cu is acid-soluble. It is essential for good work to have just the right amount of air in addition to maintaining a correct temperature. At  $340^{\circ}$  C. the S begins to burn, the temperature of the ore rises to  $400^{\circ}$  C. and makes it necessary to diminish and then to shut off the naphtha flames. The air to be admitted is regulated by the damper, the amount necessary being indicated by the temperature of the charge. The metals Fe and Cu are sulphatized at the same time; but  $\text{FeSO}_4$  is changed at  $480^{\circ}$  C. into  $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3$ , and this is decomposed at  $560^{\circ}$  C., while  $\text{CuSO}_4$  changes at  $670^{\circ}$  C. into  $2\text{CuO} \cdot \text{SO}_3$ , and this at  $736^{\circ}$  into  $\text{CuO}$ .

In roasting for  $\text{CuO}$ , which is done to free  $\text{CuSO}_4$  from  $\text{FeSO}_4$  (see below), the temperature is held between 590 and  $610^{\circ}$  C.

A charge of 3 tons of roasted ore is leached with 6-7 cbm. (212-247 cu. ft., 1585-1850 gal.)  $\text{H}_2\text{SO}_4$  of  $17^{\circ}$  Bé. at  $40$ - $50^{\circ}$  C. in a Hofmann vat (§ 240) 9 ft.  $10\frac{1}{8}$  in. in diameter and 5 ft.  $10\frac{1}{2}$  in. deep; the stirrer makes 24 r.p.m. In order to prevent any settling of ore, a perforated lead pipe served with compressed air is attached to the side-wall  $\frac{3}{8}$  in. above the bottom. Starting the stirrer requires 5 h.p., but 2 h.p. will keep it going. Five leaching tanks are placed in series on corresponding terraces, 3 ft.  $11\frac{1}{4}$  in. high, and are connected at the sides by pipes,  $3\frac{7}{8}$  in. in diameter, provided with valves. The clarified liquors are drawn from the bottom through the settled ore by means of a Borchers valve. This<sup>1</sup> consists, as shown in Figs. 432-433, of a suspended inverted cylindrical cup which can be raised and lowered by means of a handle. While the ore is being agitated, the cup is lowered, Fig. 432, so as to close the top of the discharge-pipe for clear liquor. When the ore has settled and the

<sup>1</sup> See also Borchers, *Metallurgie*, 1905, II, 375.

liquor become clear, the cap is raised so that the rim is in the liquor, and the discharge cock for liquor opened, Fig. 433.

Roasted ore is charged into the top vat and fresh acid run gradually into the third; the ore travels downward in five steps, and the liquor upward, being raised by means of acid-eggs. Tank No. 4 serves to wash the leached ore, and No. 5 to receive decopperized washed ore. Leaching in a tank lasts 2 hr., settling 0.5 hr. The Cu-liquor drawn from the top tank measures  $24^{\circ}$  Bé., is only slightly acid, and contains 4 per cent. Cu, 0.8–1.1 per cent.  $\text{Fe}^{++}$ , and 0.03 per cent.  $\text{Fe}^{+++}$ . It is freed from Fe by the Hofmann process (§ 240) to 0.08 per cent. Fe, in two stages of 50 hr. each, and filter pressed. The residue from the press is treated with cold dilute acid, 1.5–2 per cent.  $\text{H}_2\text{SO}_4$ , to dissolve any excess Cu and  $\text{Cu}_2\text{SO}_4$ . The Cu-solution is concentrated to  $33^{\circ}$  Bé. and crystallized; the market vitriol is 98 per cent. pure.

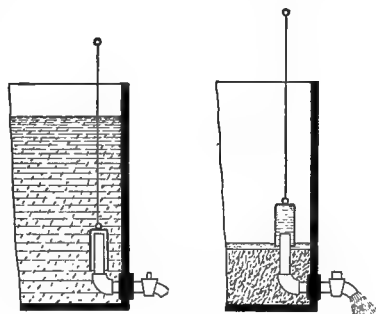
Experiments carried on at the works of the Shannon Copper Co., Clifton, Ariz., by Schimerka<sup>1</sup> with a sulphatizing roast of low-grade sulphide ore (Cu 2.37, S 3.02,  $\text{SiO}_2$  58.60, Fe 8.90,  $\text{Al}_2\text{O}_3$  13.90, CaO 2.10, MgO 2.38, Zn and Mn traces) resulted in an extraction of 84.5 per cent. of the Cu with a consumption of 3.19 lb.  $\text{H}_2\text{SO}_4$  per ton of ore.

The Bradley process<sup>2</sup> has been tried on a large scale at Anaconda. Its leading steps are sulphatizing roast, lixiviation, treatment of liquor with  $\text{CaCl}_2$ , filtration of  $\text{CaSO}_4$  from  $\text{CuCl}_2$ , precipitation of  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  by  $\text{CuO}$  or  $\text{Ca}(\text{OH})_2$ , filtration of hydroxide precipitates, and precipitation of  $\text{CuO}$  by  $\text{CaCO}_3$ . It is not in operation at present. It was found that in a chloride solution of Fe, Al, and Cu, the precipitant  $\text{CaCO}_3$  separated first  $\text{Fe}_2(\text{OH})_3$ , and then  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$  with some  $\text{Al}_2(\text{OH})_3$ .

The Hybinette process<sup>3</sup> is in operation in Norway. From 2 to 20 per cent.  $\text{Na}_2\text{SO}_4$  is added in the sulphatizing roast, the  $\text{CuSO}_4$  formed is dissolved and the Cu electrodeposited.

At the Braden copper mines<sup>4</sup> in Chile, sulphatizing in Wedge furnaces and electrodeposition of Cu is the process used for treating low-grade ores.

The sulphatization of the Cu in burnt pyrite can be accomplished by roasting in a Wedge furnace, as shown in Table 109, or a furnace with a revolving hearth, as advocated by Richard.<sup>5</sup> The same can also be accomplished with



FIGS. 432–433.—Borchers valve.

<sup>1</sup> *Eng. Min. J.*, 1913, xcvi, 1107.

<sup>2</sup> *Eng. Min. J.*, 1912, xciii, 47, 533; *Mct. Chem. Eng.*, 1912, x, 178; *Mines and Mct.*, 1912, iii, 404.

<sup>3</sup> *Mct. Chem. Eng.*, 1913, xi, 6.

<sup>4</sup> Yeatman, *Min. Sc. Press*, 1911, ciii, 769.

Editor, *op. cit.*, 1913, cvi, 932.

<sup>5</sup> *Chem. Z.*, 1912, xxxvi, 565.

spreading the ore, moistening with mother-liquor, and exposing to the sun, as advocated by Truchot. The second method has been recommended for burnt pyrite with <1.5 per cent. Cu; it is not suited for richer ore.

**217. Leaching Sulphide Ore after Conversion into Sulphate by Ferric Sulphate.**—The leading facts regarding the action of  $\text{Fe}_2(\text{SO}_4)_3$  upon  $\text{CuS}_x$  have been given in § 196. In the weathering process (§ 211–213) the copper liquor is passed over  $\text{FeS}_2$  to reduce  $\text{Fe}_2(\text{SO}_4)_3$  to  $\text{FeSO}_4$ , but  $\text{Fe}_2(\text{SO}_4)_3$  as a straight solvent for  $\text{CuS}_x$  is little used. The experiments of Austin<sup>1</sup> at Cananea form the most valuable record of the action of reagent and of its regeneration; the work of Gahl<sup>2</sup> at Morenci, Ariz., is of interest.<sup>3</sup>

At the works of the Shannon Copper Co., Clifton, Ariz., Schimerka,<sup>4</sup> the copper of oxide ore (Cu 1.90,  $\text{SiO}_2$  40.80, Fe 16.50,  $\text{Al}_2\text{O}_3$  8.40, CaO 5.80, MgO 9.60, Zn 1.30, Mn 0.70, S 0.55, Au and Ag traces) with a gangue of decomposed porphyry and altered limestone, which forbids direct treatment with  $\text{H}_2\text{SO}_4$ , is made soluble by means of  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{H}_2\text{SO}_4$  produced by moistening the ore with  $\text{FeSO}_4$  and exposing it to the  $\text{SO}_x$ -gases of a roast-heap. The  $\text{FeSO}_4$ , coming from the liquors of the precipitating troughs, is oxidized according to  $2\text{FeSO}_4 + \text{SO}_2 + \text{O}_2 + \text{catalyzing ore} = \text{Fe}_2(\text{SO}_4)_3$ ; this salt is reduced again in part by  $\text{SO}_2$ , viz.,  $\text{Fe}_2(\text{SO}_4)_3 + \text{SO}_2 = 2\text{FeSO}_4 + 2\text{SO}_3$ . In working, 1000 tons of 2-in. oxide ore is piled upon 100 tons of pyrite to a circular heap, and covered with a layer of fines 1 ft. thick; flues in the pyrite, and chimneys in the oxide ore serve for kindling and for regulating the roast. In well-roasted ore as much as 85–96 per cent. of the Cu is water-soluble; the extractions range from 72 to 82 per cent., but are much lower with ore which has not been well roasted. The ore is leached in charges of 75 tons in tanks, 25 ft. in diameter and 5 ft. deep, having a false bottom of wooden strips 2 in. high and 1 in. wide covered with cocoa matting. The Cu is precipitated with scrap iron in launders 300 ft. long, 5 ft. wide and 2 ft. deep; the effluent liquor contains up to 9.5 per cent.  $\text{FeSO}_4$ .

**218. Siemens-Halske Process.**<sup>5</sup>—Siemens and Halske<sup>6</sup> in 1886 devised their process, which consists of two operations:

(1) Leaching raw or rough-roasted S-ide ore with a solution of  $\text{Fe}_2(\text{SO}_4)_3$  containing some free  $\text{H}_2\text{SO}_4$ , whereby Cu is converted into  $\text{CuSO}_4$ , and the solven reduced to  $\text{FeSO}_4$ .

(2) Electrodepositing the Cu from the solution, using an insoluble anode and diaphragm, and at the same time regenerating the original solvent. The

<sup>1</sup> *Mines and Metl.*, 1910, II, 5.

<sup>2</sup> *Met. Chem. Eng.*, 1912, X, 306; *Tr. Am. Electrochem. Soc.*, 1914, XXV.

<sup>3</sup> J. Irving (Austin, *Min. Sc. Press*, 1914, CVIII, 77) patented a process in which  $\text{Fe}_2(\text{SO}_4)_3$  is the solvent.

<sup>4</sup> *Eng. Min. J.*, 1913, XCVI, 1107.

<sup>5</sup> *Eng. Min. J.*, 1892, LIII, 327.

Wedding, *Verh. Verein. Beförd. Gewerbesleiss.*, 1892, LXXI, 129; *Berg. Hüttenm. Z.*, 1892, LI, 187; *Stahl u. Eisen.*, 1892, XII, 315; *Rev. Un. Min.*, 1892, XVII, 158.

Cohen, *Berg. Hüttenm. Z.*, 1894, LIII, 328; *Oest. Zt. Berg. Hüttenw.*, 1894, XLII, 432; *Zt. Electrochemie*, 1894, I, 53.

<sup>6</sup> Borchers-McMillan, "Electric Smelting and Refining," 1904, 260.



solution is expressed by  $x\text{H}_2\text{SO}_4 + \text{Cu}_2\text{S} + 2\text{Fe}_2(\text{SO}_4)_3 = x\text{H}_2\text{SO}_4 + 2\text{CuSO}_4 + 4\text{FeSO}_4 + \text{S}$ ; the electrodeposition by  $x\text{H}_2\text{SO}_4 + \text{CuSO}_4 + 2\text{FeSO}_4 = x\text{H}_2\text{SO}_4 + \text{Cu} + \text{Fe}_2(\text{SO}_4)_3$ . The process does not appear to have met with success. While calculation shows that the electromotive force necessary to overcome the resistance is low, 0.38 volt, the complexity of the apparatus, the necessity of a diaphragm which increases the resistance and lasts only a short time, the use of carbon-rod anodes which disintegrate quickly in S-ate solutions, the difficulty of clarifying turbid liquors, etc., have made the process too costly.

### 219. Leaching Sulphide Ore after Conversion into Oxide by Roasting.—

The roasting of S-ide ore that is to be leached has to be carried on at a low temperature in order to prevent the formation of silicate and ferrite, both of which are not readily dissolved. If the temperature of 450–480° C. recommended by Thomas<sup>1</sup> be maintained, the Cu will be present mainly as  $\text{CuSO}_4$ ; if it be much exceeded to form  $\text{CuO}$ , there is danger of the Cu becoming insoluble. At Anaconda, Mont., Laist<sup>2</sup> erected an 80-ton leaching plant for treating the tailings from the concentrator. The roasting is carried on in a 20-ft. six-hearth Mac-Dougall furnace having a water-cooled bottom-hearth to reduce the temperature of the calcines sufficiently to permit dropping them onto a conveyor delivering to the leaching vats, 32 ft. in diameter and 12 ft. deep. There are two fire-places, the gases of which enter the furnace between the roof of the third and the floor of the second hearth. The shaft and arms of hearths 1–4 are air-cooled, those of 5–7 are not cooled. The upper three hearths serve to oxidize the S-ide mineral and are held at 540–650° C.; on the fourth hearth 1 per cent.  $\text{NaCl}$  is added to chloridize the Ag and incidentally a small amount of Cu, the Cu having been converted mostly into  $\text{CuO}$  before the  $\text{NaCl}$  is added; the temperature of the fourth hearth is not allowed to exceed 540° C. The blades of one rabble-arm on hearths 4–6 have been removed in order to do less stirring and to work with a thicker bed of ore, both of which are favorable to chloridation.

A Cottrell electric condensation apparatus<sup>3</sup> has given a recovery of 90 per cent. of the volatilized metal in properly cooled gases.

Tests with oxidation alone were not quite satisfactory. Feeding at the rate of 65–67 tons of wet tailing with 0.5 per cent. Cu in 24 hr. gave water- and acid-soluble Cu 80–83 per cent. and Ag 50–55 per cent. With the combined oxidizing and chloridizing roast the yield was Cu 85 and Ag 94 per cent. The temperatures were as follows: Floor I, 71° C.; II, 282°; III, 693°; IV, 571°; V, 450°; VI, 326°, flue 249°; calcine in hopper 277° C.

An estimate of cost shows that with 3000 tons of sands and slime per day, in the proportion of 4 : 1, the outlay per ton will be 70 cents.

More recent work<sup>4</sup> has shown that with an oxidizing roast alone 84 per cent. of the Cu, and 75 per cent. of the Ag, are extracted with a solvent containing 8 per cent.  $\text{H}_2\text{SO}_4$  and 10 per cent.  $\text{NaCl}$ , provided the flame enters

<sup>1</sup> *Metallurgic*, 1904, 1, 8, 39, 59.

<sup>2</sup> *Tr. A. I. M. E.*, 1913, XLVI, 362; U. S. Patent, No. 1076833, Oct. 13, 1913.

<sup>3</sup> Hofman, "General Metallurgy," 1913, 858.

<sup>4</sup> Laist, Letter, March 6, 1914.

the furnace on the third hearth from the top, and the temperature of the fourth hearth does not exceed  $485^{\circ}\text{C}$ . The furnace treats at present in 24 hours 100 tons tailing (dry) containing about 0.65 per cent. Cu and 2.7 per cent. S. A sample of 200 g. roasted tailing treated with the solvent for 2.5 hours at  $85^{\circ}\text{C}$ . gives a residue with 0.07 per cent. Cu, of which 0.05 per cent. is soluble in  $\text{HNO}_3$ , and 0.02 per cent. is HF. In the 400-ton leaching-tanks, the residue from the upper 5 ft. assays 0.08–0.09 per cent. Cu, that from the lower 5 ft., 0.10 per cent.

The processes discussed in §204 and following find application here.

**220. Leaching Sulphide Ore after Conversion into Chloride by Ferric Chloride.**<sup>1</sup>—This method of treatment has rarely given any satisfactory result in actual work; the recent laboratory experiments of Froelich appear promising, but the proceeding as a whole cannot well become general, and will be applied only in special cases.

**221. Doetsch and Froelich Processes.** 1. THE DOETSCH PROCESS.—This process<sup>2</sup>, once practised at Rio Tinto and Tharsis, Spain, aims to convert  $\text{CuS}_x$  by means of  $\text{FeCl}_3$  into soluble  $\text{CuCl}_x$  with the formation of  $\text{FeCl}_2$ , to precipitate the Cu with Fe, and to regenerate the solvent by means of Cl. The ore, crushed to hazelnut size, is piled up in heaps, 49 ft.  $2\frac{3}{8}$  in. square and 13 ft.  $1\frac{1}{2}$  in. high, and at the same time the necessary mixture of  $\text{Fe}_2(\text{SO}_4)_3$  and NaCl added to form  $\text{FeCl}_3$ . The heap is wetted, when  $\text{FeCl}_3$  forms— $\text{Fe}_2(\text{SO}_4)_3 + 6\text{NaCl} + x\text{H}_2\text{O} = 2\text{FeCl}_3 + 3\text{Na}_2\text{SO}_4 + x\text{H}_2\text{O}$ . This is allowed to act some time upon the ore, when reactions  $\text{Cu}_2\text{S} + 4\text{FeCl}_3 + x\text{H}_2\text{O} = 2\text{CuCl}_2 + 4\text{FeCl}_2 + x\text{H}_2\text{O} + \text{S}$  and  $\text{CuS} + 2\text{FeCl}_3 + x\text{H}_2\text{O} = \text{CuCl}_2 + 2\text{FeCl}_2 + \text{S} + x\text{H}_2\text{O}$  take place.

After some time the ore is leached and the Cu precipitated by Fe:  $\text{CuCl}_2 + 2\text{FeCl}_2 + \text{S} + x\text{H}_2\text{O} + \text{Fe} = \text{Cu} + 3\text{FeCl}_2 + \text{S} + x\text{H}_2\text{O}$  and  $2\text{CuCl} + 2\text{FeCl}_2 + \text{S} + x\text{H}_2\text{O} + \text{Fe} = 2\text{Cu} + 3\text{FeCl}_2 + \text{S} + x\text{H}_2\text{O}$ . The mother liquor is raised to the top of a tower filled with coke where, trickling down, it meets ascending Cl-gas, which converts  $\text{FeCl}_2$  into  $\text{FeCl}_3$  as shown by  $2\text{FeCl}_2 + \text{Cl}_2 + x\text{H}_2\text{O} = 2\text{FeCl}_3 + x\text{H}_2\text{O}$ . The Cl is generated in a reverberatory furnace by heating  $\text{FeSO}_4$  and NaCl with free access of air:  $6\text{FeSO}_4 + 3\text{O} = 2\text{Fe}_2(\text{SO}_4)_3 + \text{Fe}_2\text{O}_3$ ;  $2\text{FeSO}_4 + 4\text{NaCl} + 3\text{O} = \text{Fe}_2\text{O}_3 + 2\text{Na}_2\text{SO}_4 + 4\text{Cl}$ , and  $\text{Fe}_2(\text{SO}_4)_3 + 6\text{NaCl} + 3\text{O} = \text{Fe}_2\text{O}_3 + 3\text{Na}_2\text{SO}_4 + 6\text{Cl}$ . As in the decomposition of NaCl there is always formed some HCl, there is placed pyrolusite near the flue end of the furnace in order to decompose it:  $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$ . Ore with Cu 2.68 per cent. yields in four months 50 per cent. of the metal, in two years an additional 32 per cent. or 82 per cent. in all.

<sup>1</sup> Cammerer, *Berg. Hüttenm. Z.*, 1891, I, 201, 262.

<sup>2</sup> Editor, *Eng. Min. J.*, 1882, XXXIV, 163; *Berg. Hüttenm. Z.*, 1882, XLVI, 461.

Launay, *Ann. Min.*, 1889, XVI, 498; *Berg. Hüttenm. Z.*, 1890, XLIX, 229; *Eng. Min. J.*, 1890, I, 741.

Deumié, *Bull. Soc. Ind. Min.*, 1887, I, 858; *Berg. Hüttenm. Z.*, 1888, XLVII, 292.

Cummence-Wimmer, *op. cit.*, 1883, XLII, 292.

Collins, *Tr. Inst. Min. Met.*, 1893–94, II, 23.

Francke, *Metallurgie*, 1910, VII, 487.

Mengler, *op. cit.*, 1911, VIII, 178.

2. THE FROELICH PROCESS.<sup>1</sup>—Here a half-concentrated solution of  $\text{FeCl}_3$  at  $70\text{--}80^\circ \text{C.}$  is circulated for a maximum of three days in the steam-jacketed agitating vessel shown in Fig. 434, when  $\text{CuS}_x$  is converted solely into  $\text{CuCl}_2$  no  $\text{Cu}_2\text{Cl}_2$  being formed; the Cu is precipitated in a short time in a second vessel of the same construction; and the  $\text{FeCl}_2$  regenerated with air in a third. This agitating vessel, which is in operation in industrial chemical plants<sup>2</sup> and resembles the Hendryx agitator used in cyaniding,<sup>3</sup> is a steam-jacketed cylindrical vat, *t*, Fig. 434, with hopper-shaped bottom holding the ore *E*. At the center is suspended an earthenware or wooden cylinder, *c*, with inlets, *b*, and outlets, *o*, in which rotates at high speed a screw propeller, *s*, to raise the solvent from near the bottom and discharge it at the top. With vessels of 777, 2190, and 2825 cu. ft. capacity, the horsepower required is said to be 15, 33, and 51, if the propeller makes 450 r.p.m. Table 110 gives the extractions obtained on a laboratory scale.

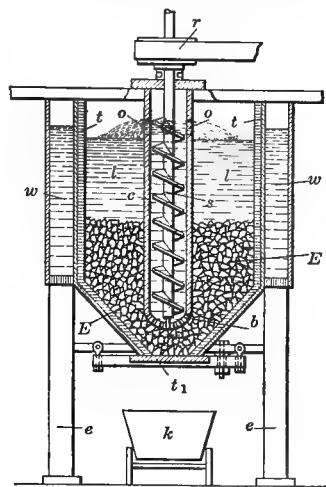


FIG. 434.—Froelich agitating vat. *t*, Vessel; *t'*, trap-door; *E*, ore; *c*, stirring cylinder; *b*, inlet and *o* outlet for *l* the  $\text{FeCl}_3$ -liquor; *s*, screw propeller; *w*, steam jacket; *r*, driving belt; *e*, supporting column; *k*, tailings car.

TABLE 110.—YIELD OF CU FROM SULPHIDE MINERALS WITH  $\text{FeCl}_3$  IN A FROELICH AGITATOR

Ore	Size, mm.	Time of leaching, hr.	Cu in ore, per cent.	Cu in tailing, per cent.	Extraction, per cent.
Chalcocite.....	Powder	15.5	0.94	0.02	98
Chalcocite.....	15	24	0.52	0.13	76
Chalcocite.....	10	66.5	7.6	0.51	93
Chalcocite.....	4	9	7.8	1.09	86
Chalcopyrite....	Powder	24.5	7.8	Small	Nearly 100
Chalcopyrite....	Powder	36	16.7	0.53	97
Tetrahedrite....	Powder	9	22.7	15.1	34

Heating chalcopyrite in a closed vessel to  $200^\circ \text{C.}$  causes decomposition:  $2 \text{CuFeS}_2 = \text{Cu}_2\text{S} + 2\text{FeS} + \text{S}$ , which makes the mineral readily soluble; tetrahedrite gives an unsatisfactory yield. The precipitation is accomplished in one-twenty-fourth the time taken by the common method, and the cement Cu is granular and little contaminated with impurities. The regeneration of  $\text{FeCl}_2$  by means of air according to  $6\text{FeCl}_2 + \text{O}_3 = \text{Fe}_2\text{O}_3 + 4\text{FeCl}_3$ , is claimed by the inventor to be complete. It would appear that insoluble oxychlorides ought to form which

<sup>1</sup> Froelich, *Metallurgie*, 1908, v, 206; *Electrochem. Zt.*, 1908-09, xv, 163; *Zt. für Chemische Apparatenkunde*, 1908, III, 65.

<sup>2</sup> *Austin, Mines and Methods*, 1910, II, 68, 119.

<sup>3</sup> *Archimedian Screw Agitator*, G. E. Davis, "Handbook of Chemical Engineering," Davis Bros. Manchester, 1904, II, 151.

<sup>4</sup> Hofman, *General Metallurgy*, 1913, p. 714.

would cause a loss of Fe and of Cl. If the regeneration by air were assisted by the admission of some electrolytic Cl, the formation of oxychlorides would be diminished, and the amount of  $\text{FeCl}_3$  in the solution kept approximately constant (Austin.)

The Slater process<sup>1</sup> is based upon the dissolving action of  $\text{FeCl}_3$ .

**222. Leaching Sulphide Ore after Conversion into Chloride by Cupric Chloride. HÖEPLNER PROCESS.**—The only process to be considered is that of Höepfner<sup>2</sup>, patented in 1888. It consists of two operations:

(1) Dissolving finely-crushed raw or rough-roasted ore in a hot solution of  $\text{CuCl}_2$  in brine, whereby the  $\text{CuCl}_2$  is reduced to  $\text{Cu}_2\text{Cl}_2$ , and the  $\text{CuS}$  of the ore converted into  $\text{Cu}_2\text{Cl}_2$ ;

(2) Dividing the solution into two equal parts, and passing one-half through the cathode- and the other through the anode-compartment of an electrolytic cell with parchment diaphragm.

(3) Depositing Cu on the sheet-copper cathode, and setting free Cl at the carbon anodes, which converts the  $\text{Cu}_2\text{Cl}_2$  of the anode-division into  $\text{CuCl}_2$ . The two solutions combined after leaving the cell will form a regenerated solvent of  $\text{CuCl}_2$  with half the Cu it contained when entering the cell. Solution may be expressed by  $\text{NaCl} + \text{CuCl}_2 + \text{CuS} = \text{NaCl} + \text{Cu}_2\text{Cl}_2 + \text{S}$ ;  $\text{NaCl} + 2\text{CuCl}_2 + \text{Ag}_2\text{S} = \text{NaCl} + \text{Cu}_2\text{Cl}_2 + 2\text{AgCl} + \text{S}$ ; and electrodeposition by  $\text{NaCl} + \text{Cu}_2\text{Cl}_2 = \text{NaCl} + 2\text{Cu} + \text{Cl}_2$ . A cell is estimated to absorb about 0.8 volt. The process has not proved successful on account of the difficulties encountered in getting the Cu into solution, and the short life of both the diaphragm and the anodes. Cohen and Lenz<sup>3</sup> did away with the diaphragm by a special arrangement of apparatus; this also reduced the electromotive force necessary to < 0.5 volt. There remain the imperfect extraction of the Cu from the ore and the corrosion of the carbons.

**223. Leaching of Sulphide Ore after Oxidizing, —Roasting, and Chlorinating by Ferrous or Calcium Chloride.**—The two processes belonging to this heading are the Hunt and Douglas No. I and No. II.

(1) THE HUNT AND DOUGLAS PROCESS NO. I.<sup>4</sup> This regenerative process is

<sup>1</sup> Editor, *Eng. Min. J.* 1913, xcvi, 595; Morse, *Min. Sc. Press.*

<sup>2</sup> Eilers, *Eng. Min. J.*, 1892, liii, 471.

Wedding, *Verh. Verein. Beförd. Gewerbefleiss.*, 1892, lxxi, 133; *Berg. Hüttenm. Z.*, 1892, xlvi, 188; *Stahl u. Eisen*, 1892, xii, 315; *Rev. Un. Min.*, 1892, xvii, 159.

Höepfner, *Zt. angew. Chem.*, 1891, 160; *Min. Ind.*, 1893, ii, 285.

Cohen, *Zt. Electrochem.*, 1895, ii, 25.

Editor, *Eng. Min. J.*, 1896, lxxii, 584.

Raschig, F. "Action of  $\text{CuCl}_2$  upon Met S," Dissertation, Berlin, 1885.

Borchers-McMillan, "Electric Smelting and Refining," 1904, 266.

Thompson-Hamilton, "Electric Conductivity of  $\text{CuCl}_2$ , *Met. Chem. Eng.*, 1910, viii, 347.

<sup>3</sup> *Zt. Electrochem.*, 1895, ii, 25.

<sup>4</sup> Hunt, *Tr. A. I. M. E.*, 1871-73, i, 258; 1875-76, iv, 327; 1881-82, x, 11.

Olcott, *op. cit.*, 1874-75, iii, 394.

Hauch, *Oest. Zt. Berg. Hüttenw.*, 1876, xxiv, 488; *Berg. Hüttenm. Z.*, 1877, xxxvi, 308.

Stahl, *op. cit.*, 1891, i, 13.

Francke, *Metallurgie*, 1910, vii, 486.

Mengler, *op. cit.*, 1911, viii, 177.

based upon the chloridizing effect of a neutral solution of  $\text{FeCl}_2$  in hot ( $70^\circ \text{C.}$ ) brine upon pulverized oxide copper ore or sulphide ore which has been subjected to a complete oxidizing roast. The chemical reaction taking place is  $3\text{CuO} + 2\text{FeCl}_2 + (x+3)\text{H}_2\text{O} + y\text{NaCl} = 2\text{CuCl} + \text{CuCl}_2 + 2\text{Fe}(\text{OH})_3 + x\text{H}_2\text{O} + y\text{NaCl}$ . In the presence of  $\text{Cu}_2\text{O}$  there is separated Cu according to  $3\text{Cu}_2\text{O} + 2\text{FeCl}_2 + (x+3)\text{H}_2\text{O} + y\text{NaCl} = 4\text{CuCl} + \text{Cu}_2 + 2\text{Fe}(\text{OH})_3 + x\text{H}_2\text{O} + y\text{NaCl}$ . This Cu might act upon  $\text{CuCl}_2$  as shown by  $\text{Cu} + \text{CuCl}_2 + x\text{H}_2\text{O} + y\text{NaCl} = 2\text{CuCl} + x\text{H}_2\text{O} + y\text{NaCl}$ ; but experience has shown that it is advisable to convert by roasting any  $\text{Cu}_2\text{O}$  present into  $\text{CuO}$  before leaching. The action of  $\text{FeCl}_2$  upon  $\text{CuO}$  overheated in roasting is imperfect; a similar behavior with  $\text{Fe}_2(\text{SO}_4)_3$  has been noted by Thomas.<sup>1</sup> The  $\text{FeCl}_2$  is prepared by dissolving 120 lb.  $\text{NaCl}$  in 1000 lb.  $\text{H}_2\text{O}$ , adding 280 lb.  $\text{FeSO}_4 + \text{aq.}$  to the solution, and giving 200 lb. more of  $\text{NaCl}$ . The reaction taking place is:  $\text{FeSO}_4 + (y+2)\text{NaCl} + x\text{H}_2\text{O} = \text{FeCl}_2 + \text{Na}_2\text{SO}_4 + y\text{NaCl} + x\text{H}_2\text{O}$ ;  $\text{Na}_2\text{SO}_4$  falls out of solution and is removed. The Cu chlorides formed by the action of  $\text{FeCl}_2$  are separated from the  $\text{Fe}(\text{OH})_3$  by filtration and brought in contact with metallic Fe to precipitate Cu according to  $2\text{CuCl} + \text{CuCl}_2 + x\text{H}_2\text{O} + y\text{NaCl} + 2\text{Fe} = 3\text{Cu} + 2\text{FeCl}_2 + x\text{H}_2\text{O} + y\text{NaCl}$ .

The process is not in operation although it has been tried at several places. The interest in it is therefore mainly chemical. The advantages are, absence of chloridizing roast; use with calcareous ores; and small consumption of fuel and Fe; the disadvantages, low extraction of copper (tailings assay Cu 0.5 per cent.); loss of Cl by the formation of basic salts [ $6\text{FeCl}_2 + x\text{H}_2\text{O} + y\text{NaCl} + 3\text{O} = (4\text{FeCl}_3 + \text{Fe}_2\text{O}_3) + x\text{H}_2\text{O} + y\text{NaCl}$ ], and by included  $\text{CuO}$  or  $\text{CuCl}_2$ ; difficulty of filtration of  $\text{Fe}(\text{OH})_3$  and of basic salts; and precipitation of part of the dissolved Ag by Cu.

(2) THE HUNT AND DOUGLAS PROCESS NO. II.<sup>2</sup>—This process, also regenerative, is based upon the following:

(1) The solution of  $\text{CuO}$  in  $\text{H}_2\text{SO}_4$ , viz.,  $\text{CuO} + \text{H}_2\text{SO}_4 + x\text{H}_2\text{O} = \text{CuSO}_4 + (1+x)\text{H}_2\text{O}$ .

(2) The partial chlorination of  $\text{CuSO}_4$  by  $\text{FeCl}_2$  or  $\text{CaCl}_2$ , viz.,  $2\text{CuSO}_4 + \text{FeCl}_2 + x\text{H}_2\text{O} = \text{CuSO}_4 + \text{CuCl}_2 + \text{FeSO}_4 + x\text{H}_2\text{O}$  or  $2\text{CuSO}_4 + \text{CaCl}_2 + x\text{H}_2\text{O} = \text{CuSO}_4 + \text{CuCl}_2 + \text{CaSO}_4 + x\text{H}_2\text{O}$ .

(3) The formation and precipitation of  $\text{CuCl}$  by the forcing of  $\text{SO}_2$  (9 per cent. vol.) through the  $\text{CuSO}_4$ - $\text{CuCl}_2$  solution, with the simultaneous regeneration of the  $\text{H}_2\text{SO}_4$ , which is used again as solvent after the expulsion of dissolved  $\text{SO}_2$ , viz.,  $\text{CuSO}_4 + \text{CuCl}_2 + \text{SO}_2 + (x+2)\text{H}_2\text{O} = 2\text{CuCl} + 2\text{H}_2\text{SO}_4 + x\text{H}_2\text{O}$ .

(4) The regeneration of the  $\text{FeCl}_2$ , or  $\text{CaCl}_2$ , by the decomposition of  $\text{CuCl}$

<sup>1</sup> *Metallurgie*, 1904, I, 8, 39, 59.

<sup>2</sup> Hunt, *Tr. A. I. M. E.*, 1881-82, x, 11; 1887-88, xvi, 80; *Eng. Min. J.*, 1885, xl, 37. Douglas, *Min. Res. U. S.*, 1883-84, 279.

Howe, "Production Gold and Silver in the U. S.," 1883, 790.

Franke, *Metallurgie*, 1910, vii, 486.

Mengler, *op. cit.*, 1911, viii, 178.

Canby, *Eng. Min. J.*, 1911, xci, 1156.

Douglas, *op. cit.*, 1911, xcii, 51.

with Fe, or  $\text{Ca(OH)}_2$  viz.,  $2\text{CuCl} + x\text{H}_2\text{O} + \text{Fe} = 2\text{Cu} + \text{FeCl}_2 + x\text{H}_2\text{O}$  or  $2\text{CuCl} + x\text{H}_2\text{O} + \text{Ca(OH)}_2 = 2\text{Cu(OH)} + \text{CaCl}_2 + x\text{H}_2\text{O}$ .

The advantages of this modification of process No. I are: absence of  $\text{Fe}_2(\text{OH})_3$  to be filtered, low consumption of Fe, and recovery of pure Cu. The disadvantages, loss of some Ag,<sup>1</sup> and imperfect precipitation of CuCl by  $\text{SO}_2$ .

The process was used by O. Hofmann<sup>2</sup> at the Argentine works of the Kansas City Smelting and Refining Co. for treating matte with Cu 40, Pb 11, Fe 20, Zn 2, Mn 1, S 21 per cent., and Ag 250 oz. per ton. He succeeded in overcoming the many difficulties encountered, but found it advantageous to modify the process by chloridizing the  $\text{CuSO}_4$ -solution with HCl, reducing  $\text{CuCl}_2$  to CuCl with Cu, filter-pressing CuCl, decomposing it with Fe, separating  $\text{FeCl}_2$  from Cu (90–94 per cent. pure), evaporating to dryness, heating in a retort in the presence of air and steam, and recovering the HCl formed. The modified process was in operation for some time, but was replaced by the manufacture of blue vitriol (§ 240), more profitable at that time.

Other modifications are those by Stahl,<sup>3</sup> using  $\text{MgCl}_2$ ; Laist,<sup>4</sup> absorbing  $\text{SO}_2$  in a cold  $\text{CuSO}_4$ -NaCl solution and then heating in a closed vessel under pressure to form  $\text{CuCl}_2$ ; Douglas,<sup>5</sup> decomposing  $\text{Cu}_2\text{Cl}_2$  electrolytically; Cappellen-Smith, decomposing  $\text{Cu}_2\text{Cl}_2$  by heating with  $\text{Ca(OH)}_2$  and C to a low temperature,

**224. Leaching of Sulphide Ore after Chloridizing Roasting.**—Chloridation of sulphide copper with < 2.75 per cent. Cu in connection with heap-roasting used to be the common practice at Rio Tinto.<sup>6</sup> Heaps 20 by 26 ft. and 10 ft. high with 800 tons of ore, or 26 by 30 ft. with 1200 tons of ore, were built over three longitudinal and two transverse air flues, 20 in. square; the smaller heaps had two, the larger three chimneys. The ore was roasted and then leached. The leached ore was removed from the tanks, mixed with raw ore, 2–3 per cent. salt, and 2–3 per cent. pyrolusite. This mixture was now placed upon an ordinary heap to a depth of 16.5 ft., when this had been fired and  $\text{SO}_2$  was coming off freely. The chloridation then proceeded in the usual way. When the roasting was finished, the surface of the heap was divided by ridges into leaching beds 26 ft. square and watered. A leached heap was allowed to weather, and then watered at intervals to recover additional amounts of copper. The incrustated cover was broken up when necessary.

**225. Leaching of Sulphide Ore after an Oxidizing Followed by Chloridizing Roast.** LONGMAID-HENDERSON PROCESS.—This mode of procedure was in-

<sup>1</sup> Blowing hot air through dilute  $\text{H}_2\text{SO}_4$  containing small amounts of  $\text{FeSO}_4$ , CuCl, and HCl, causes first the formation of  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{CuCl}_2$ , and then of some AgCl which is dissolved by the chlorides, and later precipitated by  $\text{Cu}_2\text{Cl}_2$ .

<sup>2</sup> *Min. Ind.*, 1908, XVII, 296.

<sup>3</sup> *Zt. angew. Chem.*, 1891, IV, 24; *Iron*, 1892, XXXIX, 166; *Oest. Zt. Berg. Hüttenw.*, 1892, XL, 88; *Berg. Hüttenm. Z.*, 1892, LI, 61.

<sup>4</sup> U. S. Patent, No. 903732, Nov. 10, 1908.

<sup>5</sup> *Eng. Min. J.*, 1911, LII, 51.

<sup>6</sup> Launay, *Ann. Min.*, 1889, XVI, 502; *Eng. Min. J.*, 1890, I, 741; *Berg. Hüttenm. Z.*, 1890, XLIX, 230.

vented by Longmaid in 1842 and improved by Henderson in 1860; it goes by the name of Longmaid-Henderson process.<sup>1</sup> It is suited for burnt pyrite, quite free from gangue and running low in Cu, and is based upon the chloridizing roasting of burnt pyrite (cinder) for the conversion of Cu, and with it of any small amount of Ag and Au present, into soluble chloride, followed by the recovery of these metals from the solution by precipitation with Fe; the residual  $\text{Fe}_2\text{O}_3$  forming a valuable iron ore. A modification of the process, less important since the advent of the electrolytic refining of copper, is the precipitation of Ag and Au before the Cu, and the working-up of the two products independently.

The composition of pyrite, roasted in kilns for the production of  $\text{SO}_2$  in sulphuric-acid plants has been given on page 85. Iron is present mainly as  $\text{Fe}_2\text{O}_3$ , then follow  $\text{FeS}_2$ ,  $\text{Fe}_2(\text{SO}_4)_3$ , and  $\text{CuFeS}_2$ . Copper is present mainly as  $\text{Cu}_2\text{S}$ , then follow  $\text{CuSO}_4$ ,  $\text{CuO}$  and lastly comes  $\text{CuFeS}_2$ . The forms in which Cu is present and the respective amounts are shown in Table III.

TABLE III.—COPPER COMPOUNDS IN KILN-ROASTED PYRITE<sup>2</sup>

Sample No.	Cu, total, per cent.	Copper, per cent., present as			
		$\text{CuSO}_4$	$\text{CuO}$	$\text{Cu}_2\text{S}$	$\text{CuFeS}_2$
1	4.41	50.00	16.1	28.10	5.70
2	4.67	14.46	13.1	64.47	8.03
3	4.42	31.39	22.8	45.90	0.00
4	1.86	12.00	19.8	54.90	13.30
5	1.06	32.10	18.6	38.80	10.50
Average . . .	3.28	27.9	18.1	46.43	7.51

The burnt pyrite to be treated by the process must contain little gangue ( $< 20$ , usually  $< 10$  per cent.) as this would consume an excessive amount of salt; it should not assay over 6 per cent. Cu, as there is danger of the formation of kernels in roasting, which acts unfavorably upon chloridation (it usually contains  $< 4$  per cent.); and lastly must show 1-1.5 parts of S for every part of Cu to obtain a satisfactory percentage of  $\text{CuCl}_2$ . Any lack in S is made up by the addition of pyrite.

<sup>1</sup> Lunge, G., "Sulphuric Acid and Alkali," Gurney and Jackson, London, 1913, I, part 3, 1470-1529. Wedding-Ulrich, *Zt. Berg. Hütten. Salin. Wesen i. P.*, 1871, XIX, 298; *Berg. Hüttenm. Z.*, 1872, XXXI, 147. Bräuning, *Zt. Berg. Hütten. Salin. Wesen i. P.*, 1877, XXXV, 156. Howe, "Production Gold and Silver in U. S.," 1883, 774. Egleston, *Tr. A. I. M. E.*, 1885, XIV, 198. Schelle-Semlitsch, *Oest. Zt. Berg. Hüttenw.*, 1893, XLI, 517, 531; *Berg. Hüttenm. Z.*, 1894, LIII, 76. Stahl, *op. cit.*, 1894, LIII, 1; 1897, LVI, 185, 235, 319. Helmhacker, *Min. Sc. Press*, 1898, LXXVI, 417. Krutwig, *Rev. Un. Min.*, 1899, XLVI, 35. Clemmer, *Min. Ind.*, 1899, VIII, 197 (Comment, *Eng. Min. J.*, 1900, LXX, 361); 1900, IX, 283. Gibb, *Tr. A. I. M. E.*, 1903, XXXIII, 669. Bahlens, *Metallurgie*, 1904, I, 258. Colby, *J. I. St. Inst.*, 1906, III, 359. Lilja, *Met. Chem. Eng.*, 1910, VIII, 395. Kothny, *Oest. Jahrb.*, 1910, LVIII, 97; *Metallurgie*, 1911, VIII, 389. Franke, *op. cit.*, 1910, VII, 488. Mengler, *op. cit.*, 1911, VIII, 179.

<sup>2</sup> Kothny, *loc. cit.*

The older data of Wedding-Ulrich (*loc. cit.*) show different proportions. Complete analyses of burnt pyrite are given by Lunge (*loc. cit.*) and Schelle-Semlitsch (*loc. cit.*).

The operations to be considered are: crushing and mixing of ore and salt; chloridizing roasting; condensing of gases and vapors; leaching chloridized ore with water and tower-liquor; clarifying the copper liquor; precipitation of Cu (with Ag and Au) by Fe; washing and refining the precipitated Cu; disposition of residue (blue billy, purple ore) from leaching; disposition of waste liquor; precipitation of Ag and Au independently of Cu; results and costs.

Illustrations of older plants have been given by Wedding (Widnes, St. Helens, England), Defrance (Hemixen, Belgium), and Bräuning (Oker, Germany), and of recent plants by Clemmer (Natrona, Pa.), and Colby (Newark, N. J.).

In Figs. 435-436 are given outline sketches of a modern 60-ton Longmaid-Henderson plant. Ore, *i.e.*, roasted pyrite or cinder, and salt are received in a delivery-bin to be transferred by means of a 14-in. conveyor belt and tripper to two 100-ton cinder- and one 20-ton salt-bins. These raw materials are fed in weighed quantities to four 2-ton revolving mixers and thence discharged through chutes into two No. 4 Krupp ball mills<sup>1</sup> from which the mixed and ground pulp passes by means of conveyors or of chutes into the boat of the elevator which empties into a 60-ton storage-bin. From this the pulp passes through a chute into a second elevator which delivers into the 2-ton bin of the Wedge 5-hearth muffle furnace, detail in Fig. 446, where it is chloridized. The chloridized ore is discharged through four openings in the bottom into 1-ton cars, running on an elevated track, and delivered to the  $2 \times 7 = 14$  leaching tanks, detail in Figs. 448-449, placed in two rows. The leached ore is removed from the tanks in 3-ton buckets traveling on an overhead trolley. The copper solution is collected in the concrete copper-liquor tank, whence it is run into nine copper-precipitating tanks placed in rows of three. These tanks receive the precipitating scrap iron through overhead trolley buckets filled from a storage building. The copper precipitate is transferred onto a copper screen moving over three wash-tanks, freed from iron, washed, settled and transferred to the filter-press. The liquor freed from copper is run from the tanks into an open concrete catch-pit charged with iron, in which floating particles of copper are settled and unprecipitated ones thrown out of solution. The effluent passes over a bright piece of iron which ought not to become tarnished.

It will be noted that the sloping floors are made of reinforced concrete, and have upturned sides, in order that all drippings may be collected and conducted to a receiving pit.

**226. Crushing and Mixing of Ore and Salt.**—Pyrite roasted in coarse-ore kilns does not exceed 3 in. in size, that from fine-ore kilns 0.25 in. As it is essential for a successful chloridation that ore and salt be intimately mixed, it becomes necessary to crush the two together. The finest size is probably 8-mesh, the coarsest 4-mesh; under 8-mesh makes too many fines for satisfactory filtration in leaching, over 4-mesh causes imperfect chloridation.

<sup>1</sup> Hofman, "General Metallurgy," 1913, p. 590.



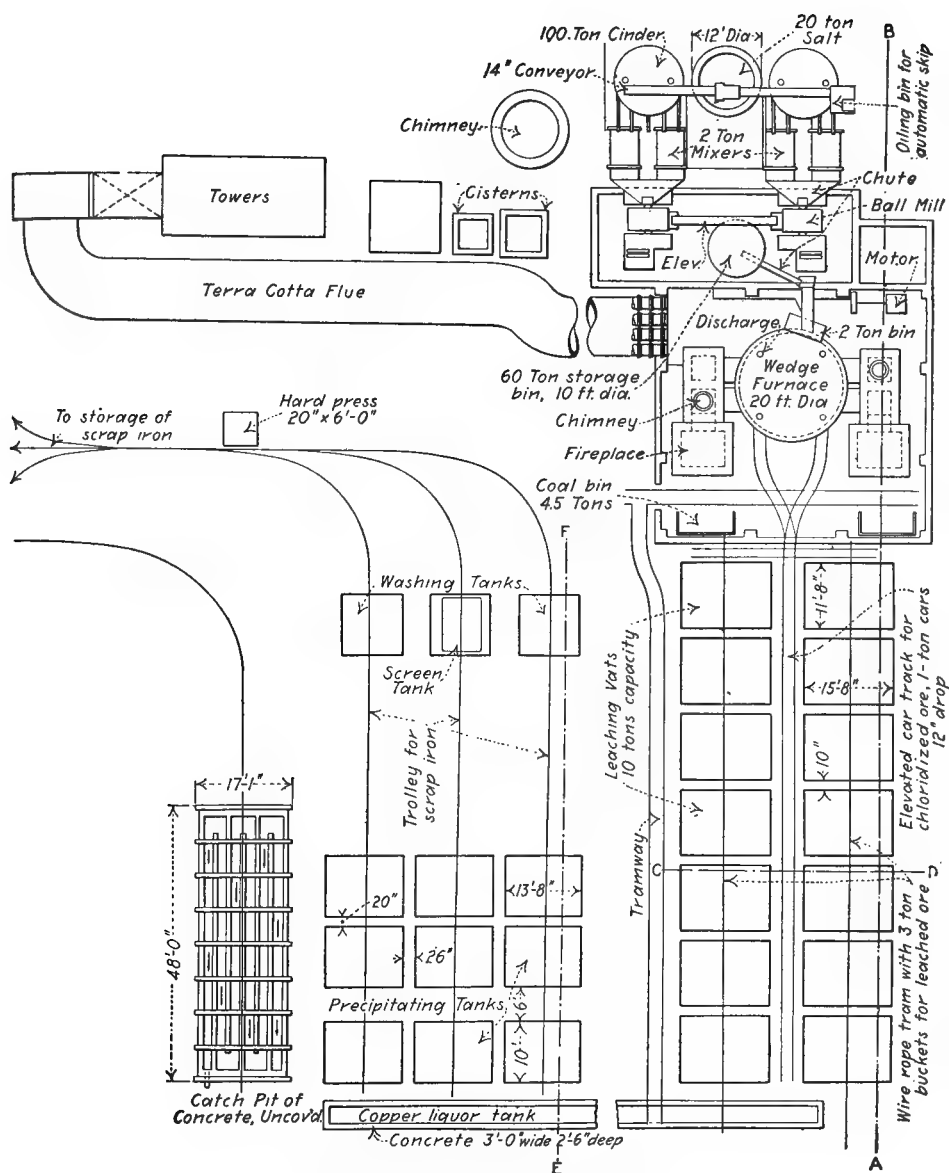


FIG. 435.—Longmaid-Henderson Plant.

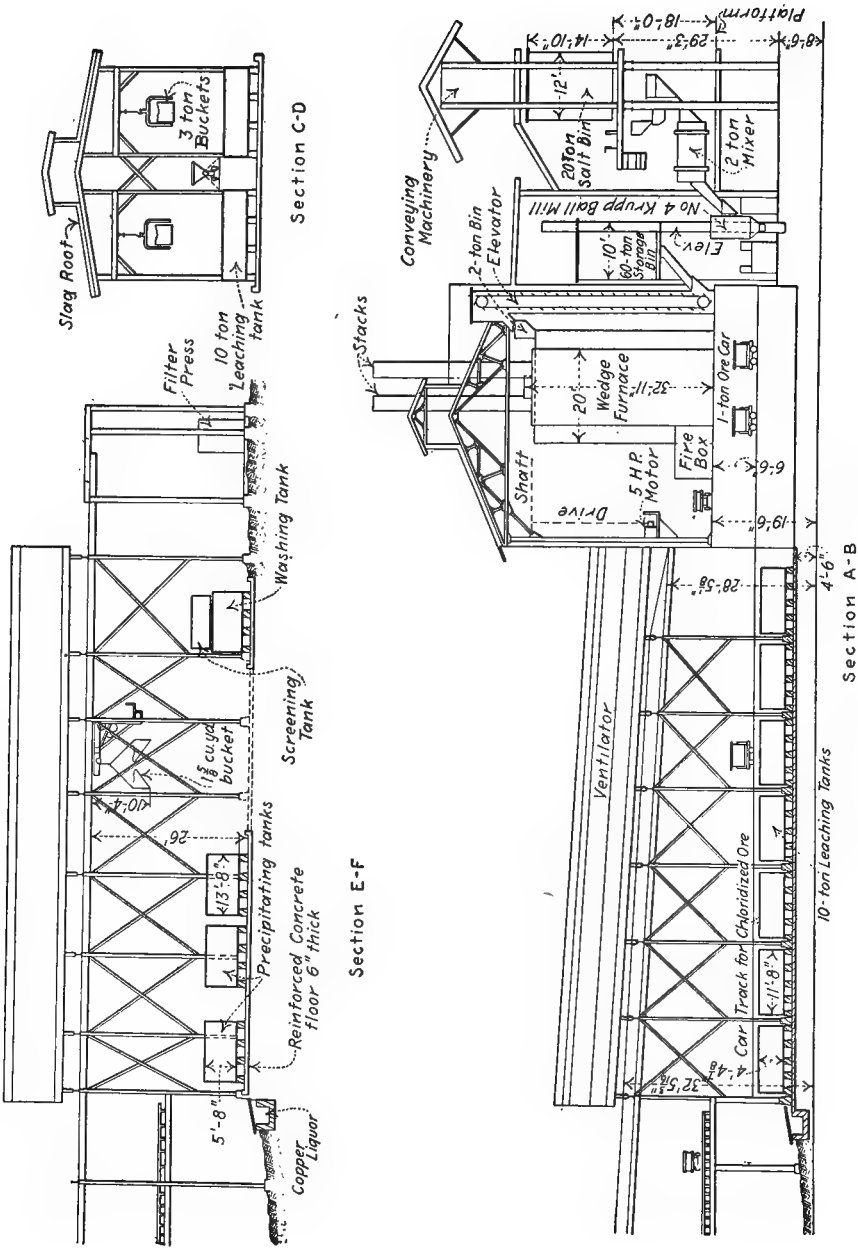
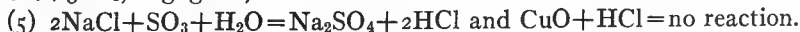
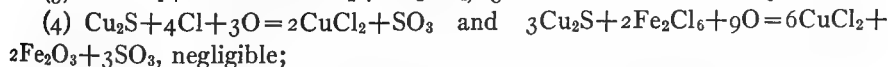
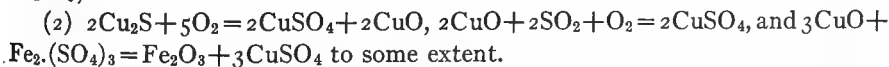
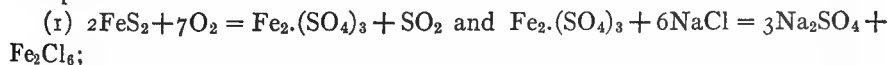


FIG. 436.—Longmaid-Henderson Plant.

Clemmer<sup>1</sup> states that the best results are obtained by crushing  $\frac{1}{3}$  of a mixture through an 8-mesh screen, the rest through a 20-mesh, and then mixing the two products. The machine commonly used is an edge-roller<sup>2</sup>; sometimes a continuous Krupp ball mill is employed. In both cases attention has to be paid to the removal of dust. An edge-roller, 9 ft. in diameter, with two runners 52 in. in diameter, weighing each 9000 lb. and making 25 r.p.m., will crush through an 8-mesh sieve in 24 hr. 100–150 tons of mixture (10 per cent. NaCl) according to moisture and coarseness of the feed; a ball mill, 6 ft.  $2\frac{1}{2}$  in. in diameter, holding 80–100 steel balls, 5 in. in diameter and smaller, weighing about 18 lb. each, and making 22 r.p.m., will treat with an 8-mesh screen in 24 hr. 100–120 tons of mixture (10 per cent. NaCl). The smallest amount of salt necessary for an ore with 4 per cent. Cu is given by Kothny (see below) as 7.5 per cent.; the largest range in practice is from 10 to 20 per cent.; the usual limit until recently was 12 and 15 per cent., when Wedge reduced it with his down-draft furnace (see below) to 9 per cent. The salt is generally not dried before using, although dried salt is easier to crush. At Oker, carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) was used to replace some of the salt in order to furnish the  $\text{H}_2\text{O}$  necessary for the formation of  $\text{HCl}$ . The crushed mixture is screened to insure uniformity.

**227. Chloridizing Roasting and Condensation of Gases.**—The chloridation of copper has been explained as being due largely to the presence in burnt pyrite of  $\text{CuSO}_4$ , which, acting upon  $\text{NaCl}$ , formed  $\text{CuCl}_2$  and  $\text{Na}_2\text{SO}_4$ , and to the decomposing effect of  $\text{FeSO}_4$ , either present as such or formed by the oxidation of  $\text{FeS}$ . The  $\text{FeSO}_4$  from both sources could act upon  $\text{NaCl}$  and form  $\text{FeCl}_2$ ,  $\text{FeCl}_3$ , and  $\text{Na}_2\text{SO}_4$ ; or, after it had been decomposed by heat, the  $\text{SO}_3$  set free would convert  $\text{Cu}_2\text{S}$  into  $\text{CuSO}_4$ ; or acting upon  $\text{NaCl}$ , it would give  $\text{Cl}$  (which would chloridize  $\text{Cu}_2\text{S}$ ) and  $\text{HCl}$  in the presence of  $\text{H}_2\text{O}$  (and chloridize  $\text{CuO}$ ). Kothny's analyses (p. 437) prove that neither  $\text{FeS}$  nor  $\text{FeSO}_4$  is present in burnt pyrite. His experiments<sup>3</sup> have shown that with burnt pyrite mixed with salt and roasted at a temperature of 500–600° C. the following reactions take place:



The  $\text{CuCl}_2$  formed may be decomposed; by  $2\text{CuCl}_2 + \text{O}_2 = 2\text{CuO} + 2\text{Cl}_2$ , a reaction which is much retarded by the presence of  $\text{Cl}$  and  $\text{HCl}$ ; by  $\text{CuCl}_2 + \text{H}_2\text{O}$

<sup>1</sup> *Min. Ind.*, 1900, IX, 283.

<sup>2</sup> The Carlin mill, Clemm, *op. cit.*, p. 284.

<sup>3</sup> *Oest. Jahrb.*, 1910, LVIII, 97; *Metallurgie*, 1911, VIII, 389.

$=\text{CuO}+2\text{HCl}$ ; by  $\text{CuCl}_2+\text{heat}=\text{CuCl}+\text{Cl}$ , which does not take place between  $350$  and  $550^\circ\text{C}$ . in the presence of much  $\text{NaCl}$ .

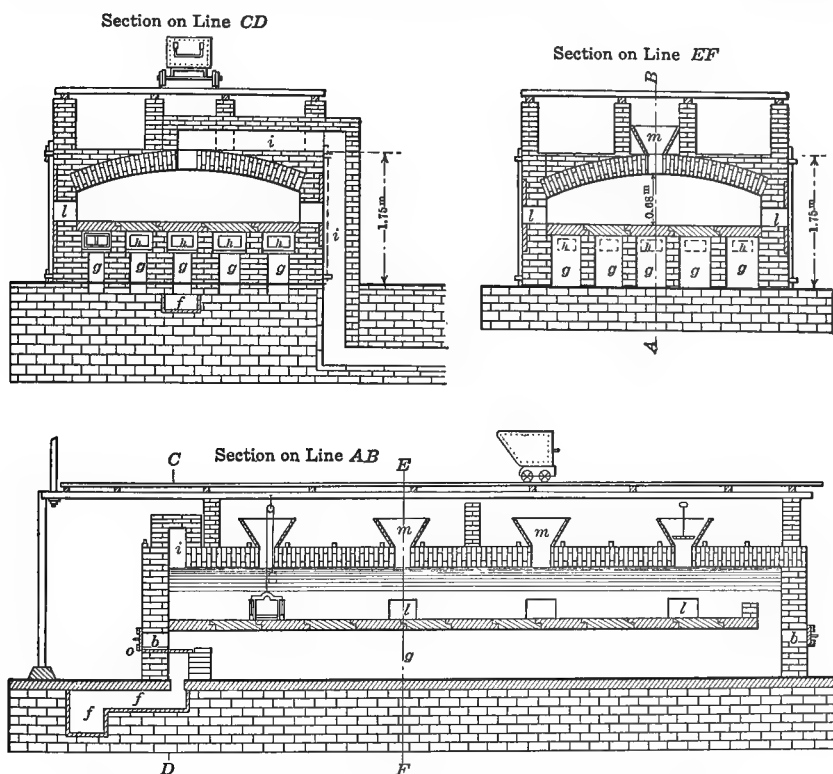
Kothny concludes that for a successful chloridizing roast it is essential: (1) that ore and salt be finely divided (8-mesh) and intimately mixed; (2) that there be free access of air and vigorous rabbling; (3) that the amount of S present be equal that of Cu; (4) that there be enough  $\text{NaCl}$  added to the charge, with 4 per cent. Cu not  $< 7.5$  per cent.  $\text{NaCl}$ ; (5) that the roast be not unnecessarily prolonged, and (6) that the temperature be held between  $500$  and  $600^\circ\text{C}$ .

Both reverberatory and muffle furnaces are used for roasting, and the ore rabbled either by hand or mechanically. The leading advantages of the reverberatory furnace are its cheapness, and the fact that it requires about half the fuel of the muffle furnace; the latter gives a more even temperature, furnishes a more concentrated gas, requiring half the condensing capacity for the towers, and has a stronger oxidizing and chloridizing effect owing to the absence of fuel gases and the consequent smaller velocity of the gas current. Most reverberatory and muffle furnaces are single-hearth; recently multiple-hearth muffle furnaces have come into use, both hand and mechanically rabbled, and have effected a considerable saving in salt. Hand-rabbled furnaces have a very small capacity, from 2, more commonly from 5 to 9 tons in 24 hr. They treat a charge weighing from 1580 to 9600 lb. in from 6 to 12 hr., the great variation being due to the percentage of Cu and the manner of operating. The new mechanical furnaces of Wedge treat about 70 tons in 24 hr. and furnish on account of the mechanical rabbling a product richer in  $\text{CuCl}_2$  than can be obtained with hand work. For the practice in the U. S., hand-rabbled furnaces need not be discussed in detail; they are fully treated by Lunge and Schelle-Semlitsch. The following examples are typical forms.

(1). THE REVERBERATORY FURNACE OF OKER.<sup>1</sup>—This is shown in Figs. 437-439. The hearth, 24 ft. long by 10 ft. wide, is built of grooved tiles; in the roof, 2 ft.  $2\frac{3}{4}$  in. high at the center, are four charging hoppers, *m*, and on either side four corresponding rabbling doors, *l*. The furnace is fired with producer gas (gaseous fuel was replaced later by solid fuel) which, arriving through *f*, passes into the distributing flue, *j*, and enters the five combustion flues, *g*, where it meets air drawn in through ports, *h*. The flame travels underneath the hearth, rises at the opposite end, where auxiliary air enters through ports *h'*, to finish the combustion and to furnish the O necessary for the oxidation of the S, and then returns passing over the ore-charge to leave the furnace through flue, *i*, leading to a gossage tower. The furnace treated two 2.5-ton charges in 24 hr., or in 24 hr. close on to 42 lb. per square foot hearth area; it required three men on a shift and consumed 10-12 per cent. coal on the chloridized ore with direct firing. A charge, crushed in an edge-roller to pass a 6-mesh screen, contained 85 per cent. burnt pyrite ( $\text{CuO}$  9.80,  $\text{Fe}_2\text{O}_3$  53.14,  $\text{FeS}_2$  7.13,  $\text{PbO}$  2.25, Ag 0.008,  $\text{ZnO}$  2.43,  $\text{Mn}_2\text{O}_3$  0.57,  $\text{SO}_3$  9.51,  $\text{Al}_2\text{O}_3$  4.43, Insol., etc., 11.65 per cent.) and 15 per cent. Strassfurt salt ( $\text{NaCl}$  85.1,  $\text{CaSO}_4$  4.0,  $\text{MgSO}_4$  3.1,  $\text{MgCl}_2$  2.6,  $\text{KCl}$  1.7,

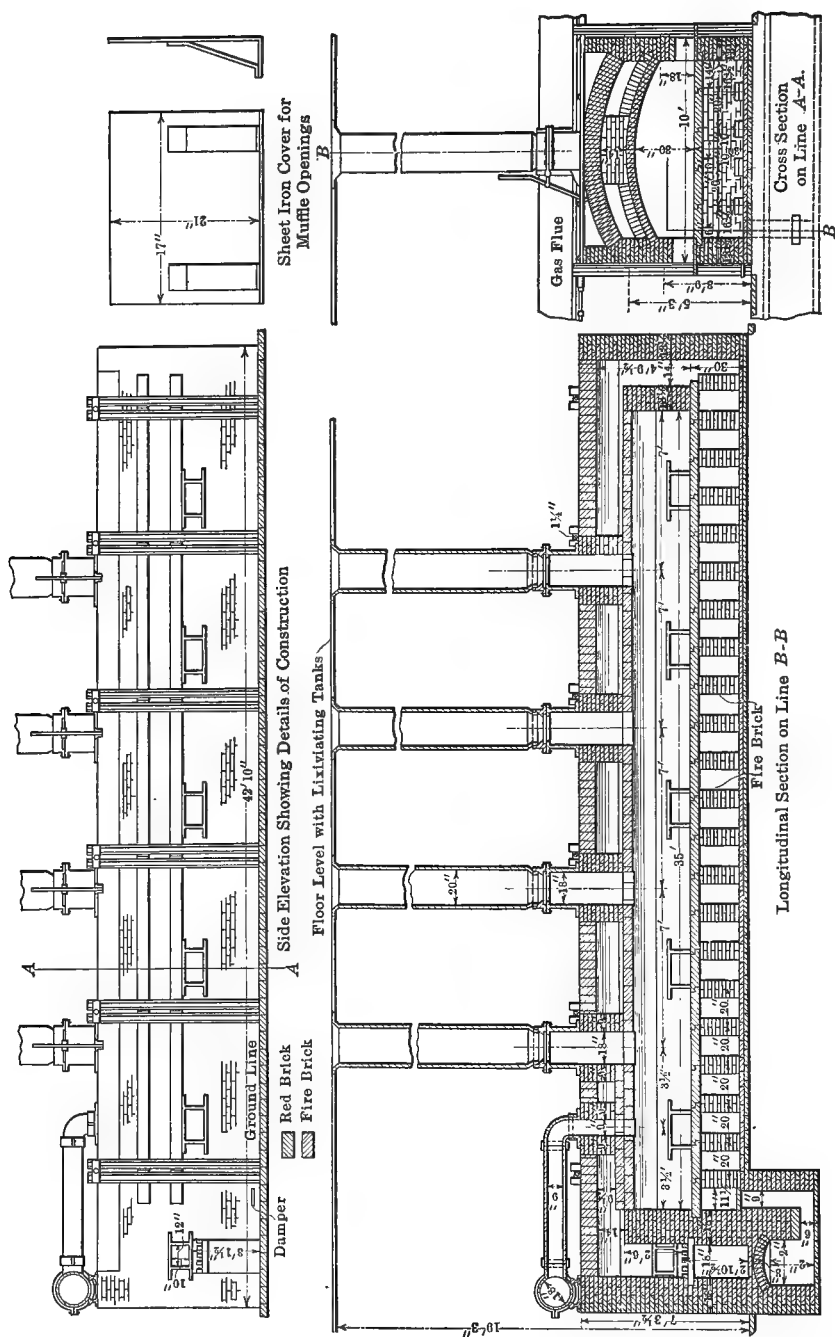
<sup>1</sup> Bräuning, *Zt. Berg. Hütten. Salin. Wesen* i. P., 1877, xxv, 156; the leaching department of the smelter has been abandoned on account of the lack of suitable ore.

$\text{HKSO}_4$  0.2,  $\text{H}_2\text{O}$  3.3 per cent.). In order to prevent overheating, the full ore-charge is not introduced at once, but in four parts. Supposing that of the four hoppers, No. 1 is near the entrance of the producer gas,  $\frac{2}{4}$  of the charge are dropped through hoppers, 2 and 3, spread to cover half the hearth, allowed to come to a dark red, whereupon whitish sulphurous fumes will pass off, and rabbled occasionally. The  $\frac{2}{4}$  are transferred to cover the hearth under hoppers 3 and 4, when the third  $\frac{1}{4}$  of the charge is dropped through hopper No. 2; and when this has become a dark red, the remaining  $\frac{1}{4}$  through hopper No. 1. Charging and



FIGS. 437-439.—Reverberatory chloridizing furnace of Oker, Germany.

bringing the charge to a uniform dark red to start the oxidation take about 4 hr. The fire is now checked, and air-flues,  $h'$ , are opened; the charge is rabbled continuously and occasionally transferred from the hotter to the cooler part of the hearth as may seem necessary. The bluish S-flame, tinged with the yellow of the  $\text{NaCl}$ , and whitish fumes gradually diminish until they disappear completely. The chloridation is finished, and the charge withdrawn and transferred to the cooling floor. During the chloridation the chemical reactions furnish most of the required heat. Toward the end more gaseous fuel is needed than at first, to keep up the necessary temperature. Bright daylight is kept from the furnace room to enable the workmen to recognize the temperature of the charge.



FIGS. 440-444.—Muffle chloridizing furnace of Natrona, Pa.

During the roast, tests are made for ascertaining the amount of  $\text{CuO}$  present by leaching a sample with boiling  $\text{H}_2\text{O}$ , filtering, boiling the residue in dilute  $\text{HCl}$ , and supersaturating with  $\text{NH}_4\text{OH}$ ; occasionally the residue from the  $\text{HCl}$  treatment is digested with  $\text{HNO}_3$  and an excess of  $\text{NH}_4\text{OH}$  added to test for undecomposed  $\text{Cu}_2\text{S}$ . The chloridized ore has a greenish-grayish color. The average chloridation result was  $\text{Cu}$  soluble in  $\text{H}_2\text{O}$  75 per cent. ( $\text{CuCl}_2$ ), soluble in dilute  $\text{HCl}$  25 per cent. ( $\text{Cu}_2\text{Cl}_2$ ,  $\text{Cu}_2\text{OCl}_2$ ,  $\text{CuO}$ ), soluble in aq. reg. 5 per cent. ( $\text{Cu}_2\text{S}$ ). In the original paper are given complete analyses of two samples of ore taken at the middle and at the end of the roast.

(2) THE MUFFLE FURNACE OF THE PENNSYLVANIA SALT MFG. CO., NATRONA, PA.<sup>1</sup> This is shown in Figs. 440-444. The hearth, 35 ft. long by 7 ft. 9 in. wide, equal to 271.25 sq. ft., is built of grooved tiles. In the roof are four feed openings served by cylindrical charge holders closed by sliding doors; on either side are five working doors. The furnace is direct-fired, the flame passes outward over the roof of the muffle, which is of double the usual thickness for a distance of 8.5 ft. to prevent overheating of charge, descends at the opposite end, returns underneath the muffle, and passes off to the chimney through an underground flue placed beneath the ash-pit. The hot roaster gases leave the muffle through cast-iron pipes joined by cast-iron bands, which are bolted together and packed with asbestos soaked in tar or a mixture of clay and tar. The furnace treats in 8 hr. a charge of 9600 lb. Spanish burnt pyrite with 2 per cent.  $\text{Cu}$ , ground through a 20-mesh sieve, and mixed with 10 per cent. salt; or in 24 hr. 106 lb. per square foot hearth area.

In a similar furnace, 22 ft. 8 in.  $\times$  13 ft. = 293.8 sq. ft., of the Tharsis works at Widnes, England,<sup>2</sup> 4500 lb. ore with 17 per cent. salt are treated in 6 hr., or in 24 hr. 61 lb. per square foot hearth area. The progress of this roast is given in Table 112. It shows that there is a decrease in the chlorida-

TABLE 112.—PROGRESS OF CHLORIDATION IN HAND-WORKED MUFFLE FURNACE OF WIDNES, ENGLAND

Percentage of total Cu	After 1 hr.	After 3 hr.	After 6.5 hr.
Soluble in $\text{H}_2\text{O}$ .....	54	51	75
Soluble in dilute $\text{HCl}$ , insoluble in $\text{H}_2\text{O}$ .....	38	42	20
Soluble only in $\text{HNO}_3$ .....	8	7	5

tion of the  $\text{Cu}$  from 54 to 51 per cent. between the first and third hour, and then a gradual increase until the maximum of 75 per cent. water-soluble  $\text{CuCl}_2$  has been reached. It may be that this decrease is accidental.

(3) THE WEDGE SINGLE-HEARTH MECHANICAL REVERBERATORY FURNACE WITH TOP MUFFLE EFFECT.—This furnace, shown in vertical section in Fig. 445, is constructed on the same principle as the pyrite burner discussed in § 69 and illustrated in Fig. 112. The furnace is 32 ft. in diameter, has a hearth 13 ft. wide corresponding to a hearth area of 768 sq. ft.; the central shaft, 4 ft. in

<sup>1</sup> Clemmer, *Min. Ind.*, 1900, IX, 287.

<sup>2</sup> Wedding, *loc. cit.*

diameter, has four water-cooled stirring arms with heavy cast-iron rables, and makes 1 rev. in 4 min.; with two arms the shaft would make 2 r.p.m. The furnace is heated with four to six oil-burners. The products of combustion and the roaster gases pass off together through the chamber covering the roof of the hearth before they enter the flue leading into the gossage tower. The burnt pyrite, crushed with 17 per cent. NaCl in an edge-roller or a ball-mill to 8-mesh, is fed mechanically near the center of the furnace and travels over the hearth in from 2 to 2.5 hr. giving a chloridation of 96 per cent. ( $\text{CuCl}_2$  40 per cent.,  $\text{Cu}_2\text{Cl}_2$ ,  $\text{CuO}$ , etc., 56 per cent.); the temperature is held at from 600 to 650° C. The furnace requires a 5-h.p. engine, consumes 11.6 gal. oil-residuum (= 178.6 lb. coal) per ton charge, and puts through in 24 hr. from 80 to 100 tons of charge.

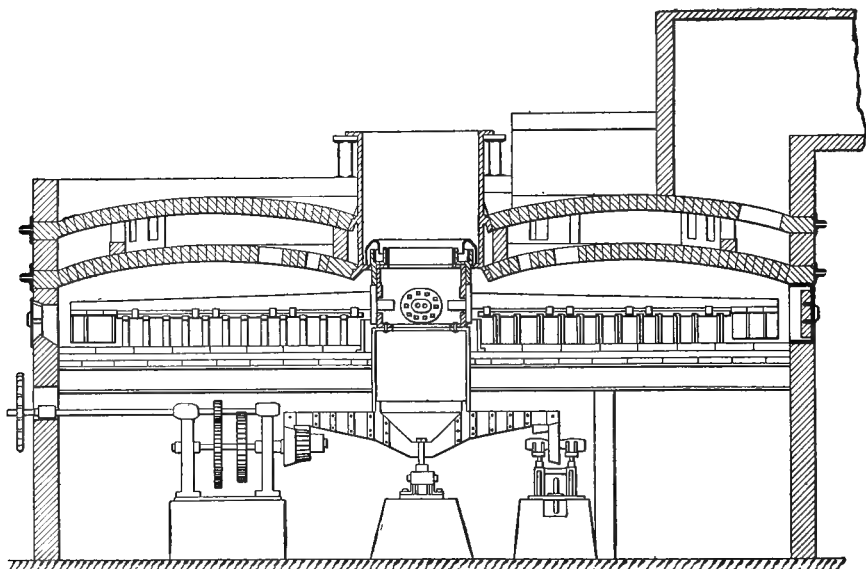


FIG. 445.—Wedge single-hearth mechanical reverberatory roasting furnace with top muffle effect.

(4) **THE WEDGE SINGLE-HEARTH MECHANICAL MUFFLE FURNACE.**—This is of the same general construction as the reverberatory furnace, with this difference: that both the upper and lower heating chambers of the muffle are heated by oil-burners, and that the fire- and roaster-gases pass off separately to the stack and the gossage tower. A muffle furnace consumes twice the fuel that does the reverberatory furnace, and the bottom is readily corroded if the chloridation is carried through on a single hearth. For this reason the reverberatory furnace is more common than the muffle furnace with a single-hearth type in spite of the great advantages the latter offers over the former as regards control of temperature and concentration of roaster-gas.

The single muffle had recently been replaced by the following furnace.

(5) **THE WEDGE MULTIPLE-HEARTH, MECHANICAL DOWN-DRAFT MUFFLE FURNACE** is shown in vertical section in Fig. 446. This is a five-hearth muffle



furnace, 18 ft. 5 in. inner diameter and 31 ft. high. The feeding and course of the ore are the same as in the Wedge pyrite burner (§ 69, Fig. 112). On account of the low temperature the rabble-arms are air cooled instead of water cooled. The leading novelty lies in the manner of firing. In the older mechanical muffle furnaces constructed upon the MacDougall principle as, *e.g.*, in the Haas furnace,<sup>1</sup> a single flame enters beneath the bottom muffle and then travels upward in zig-zag in the flues enclosing the muffles. The result is that the bottom muffle is

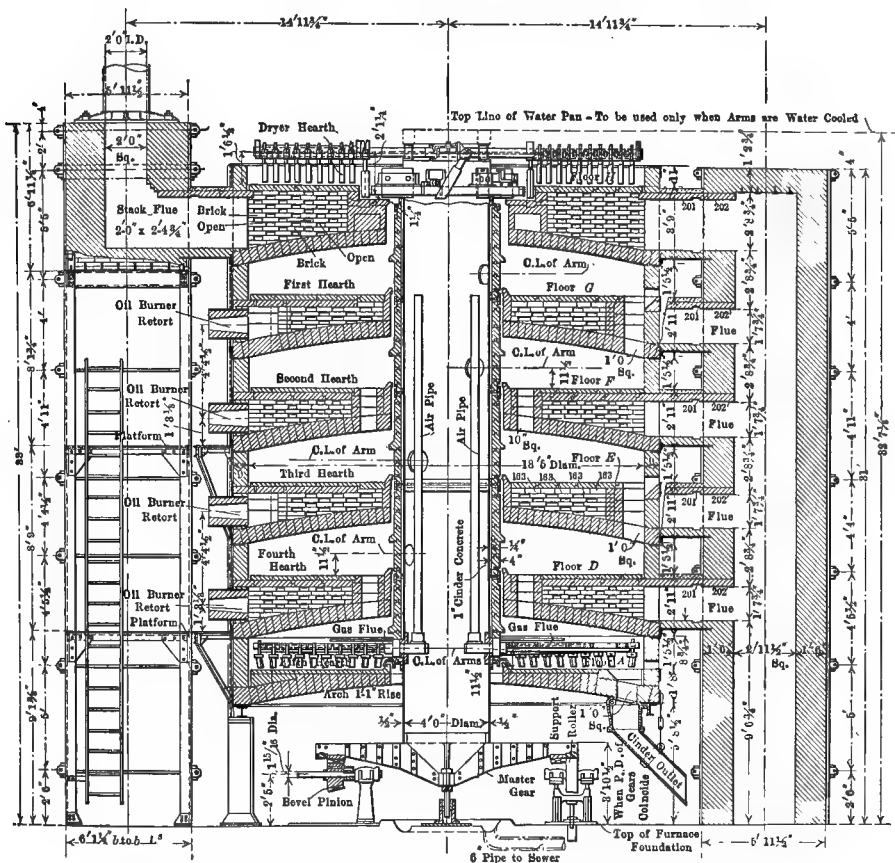


FIG. 446.—Wedge five-hearth mechanical down-draft muffle roasting furnace.

overheated, if the upper muffles are to be brought to the desired temperature; they are too cool, if the heat in the bottom muffle is correct. In the Wedge furnace each muffle is heated independently by having either oil- or gas-burners placed between the roof of one muffle and the floor of the next following, as shown in Fig. 446, or by having, with solid fuel, two fire-places on the main floor and conducting the fire-gases independently to the heating spaces between

<sup>1</sup> W. R. Ingalls, "Metallurgy of Zinc and Cadmium," Hill Publishing Co., New York, 1903, p. 143.

the muffles. In Fig. 446 are shown the oil-burners, of which there are eight; the products of combustion pass off at the right through horizontal flues into a main downtake leading to the stack. The roaster-gases zig-zag upward and pass from the top muffle into a main leading to the gossage tower. The ore passes through the furnace in 8-11 hr., being stirred by two arms on a hearth making 1 rev. in 2 min. The chloridation is 86 per cent. Cu as  $\text{CuCl}_2$ ; an additional 10 per cent. Cu or more is recovered by leaching with tower liquor. The furnace requires a 5-h.p. engine, treats in 24 hr. 60 tons of Rio Tinto burnt pyrite containing 3.5 per cent. Cu, ground through a 20-mesh sieve and mixed with 7 per cent. salt; and consumes 280 lb. bituminous coal per ton of chloridized ore, which corresponds to 18.7 gal. oil residuum.

The following is a record of burnt Spanish pyrite, crushed through a 20-mesh sieve and mixed with 10 per cent. salt, passing through the five-hearth muffle furnace.

<i>First Hearth, 375° C.</i>	{	Water—soluble	Cu. .... 0.54 per cent. = 26.09 per cent. extraction.	
		Acid—soluble	Cu. .... 0.97 “ = 46.80 “ extraction.	
		Insoluble	Cu. .... 0.56 “	
		Total	Cu. .... 2.08 per cent. = 72.89 per cent. extraction.	
<hr/>				
<i>Second Hearth, 510° C.</i>	{	Water—soluble	Cu. .... 0.66 per cent. = 31.9 per cent. extraction.	
		Acid—soluble	Cu. .... 0.95 “ = 45.8 “ extraction.	
		Insoluble	Cu. .... 0.46 “	
		Total	Cu. .... 2.07 per cent. = 77.7 per cent. extraction.	
<hr/>				
<i>Third Hearth, 560° C.</i>	{	Water—soluble	Cu. .... 1.72 per cent. = 83.5 per cent. extraction.	
		Acid—soluble	Cu. .... 0.18 “ = 8.9 “ extraction.	
		Insoluble	Cu. .... 0.16 “	
		Total	Cu. .... 2.06 per cent. = 92.4 per cent. extraction.	
<hr/>				
<i>Fourth Hearth, 620° C.</i>	{	Water—soluble	Cu. .... 1.81 per cent. = 84.6 per cent. extraction.	
		Acid—soluble	Cu. .... 0.29 “ = 13.5 “ extraction.	
		Insoluble	Cu. .... 0.04 “	
		Total	Cu. .... 2.14 per cent. = 98.1 per cent. extraction.	
<hr/>				
<i>Fifth Hearth, cooling off</i>	{	Water—soluble	Cu. .... 1.82 per cent. = 85.04 per cent. extraction.	
		Acid—soluble	Cu. .... 0.28 “ = 13.06 “ extraction.	
		Insoluble	Cu. .... 0.04 “	
		Total	Cu. .... 2.14 per cent. = 98.10 per cent. extraction.	
<hr/>				

(6) THE WEDGE MULTIPLE-HEARTH, MECHANICAL DOWN-DRAFT REVERBERATORY AND MUFFLE FURNACE.—This furnace, shown in vertical section in Fig. 447, has eight hearths over which the ore travels downward in the usual way in from 8 to 13 hr., being stirred with two arms on each hearth making 1 rev. in 2 min. as in the other furnaces of Wedge. The novel part of this furnace is the mode

of firing from two lateral fire-places. The gases from fire-place, *a*, *e.g.*, rise in the vertical flue, enter ports *e* and *f*, come in contact with the ore spread over hearths Nos. 1 and 2, heat and kindle it, and pass off into flue *b*, leading to the stack. The kindled ore is transferred onto hearth No. 3, which forms the bottom of the muffle. The heat generated by oxidation and chloridation is sufficient to make extraneous fuel unnecessary while the ore travels over hearths Nos. 3, 4, and 5. If the temperature becomes too low on hearths Nos. 6 and 7, the dampers closing the heating flues *c* and *d*, are drawn the amount required to furnish the muffles the desired amounts of heat. The gases from the six muffles pass off

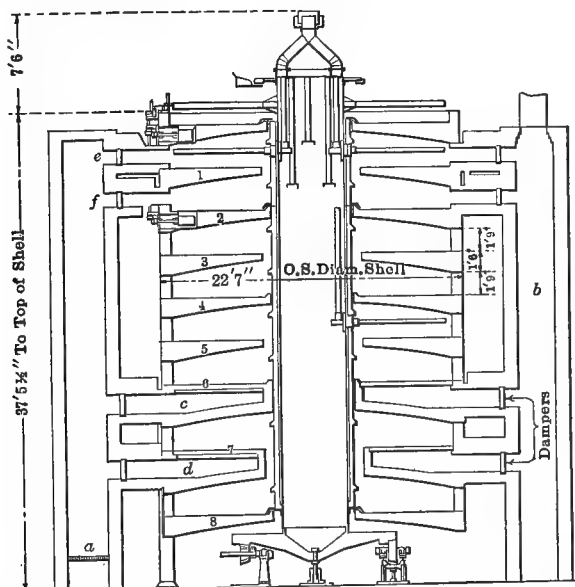


FIG. 447.—Wedge multiple-hearth Mechanical down-draft reverberatory and muffle furnace.

into the condensation tower. By the arrangement shown, the temperature of the furnace can be regulated to suit the character of the ore that is to be chloridized. With a pure Spanish pyrite the dampers of flues *c* and *d*, will remain closed, as the temperature of 500–600° C. is sufficient to obtain with a low percentage of NaCl a high chloridation. With burnt pyrite containing some blende or galena, the dampers will have to be opened more or less in order to furnish the heat necessary for the decomposition of  $\text{ZnSO}_4$  and the partial dissociation of  $\text{PbSO}_4$ .

This Wedge furnace is identical with that of Ramón and Beskow used in most of the modern European plants, the furnaces having been constructed independently on either side of the Atlantic.

(7) CONDENSATION OF GASES.—The gases issuing from a chloridizing furnace contain  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$  (from  $\text{SO}_2 + \text{Cl}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HCl}$ ), Cl, HCl, N and O, some volatilized  $\text{Cu}_2\text{Cl}_2$ , As, Sb, flue-dust, and with reverberatory

furnaces,  $\text{CO}_2$  and perhaps some  $\text{CO}$ . They ascend in a gossage tower in which water trickles down slowly absorbing the acids, condensing volatilized chlorides, and collecting particles of flue-dust. The collected water forms the "Tower Liquor" used as a solvent for  $\text{Cu}_2\text{Cl}_2$  and  $\text{CuO}$ . The gossage tower is a square or circular shell of heavy sheet lead suspended in a wooden frame or a square brick tower lined with acid-proof brick, packed in the case of muffle furnaces with coke or quartz, in the case of reverberatory furnaces with acid-proof brick laid checkerwise, as larger interstitial spaces are necessary for the greater volume of gas.

With the quickly working muffle furnaces at Natrona there is in use one tower 12 ft. square and 50 ft. high for seven furnaces having a total hearth area of 1900.75 sq. ft., or 1 sq. ft. horizontal condensing area for 13.2 sq. ft. hearth area, treating, in 24 hr., 1400 lb. ore mixture. With the slowly working reverberatory furnaces of Oker there are in use two towers 5.6 ft. square and 17.4 ft. high for three furnaces having a hearth area of 720 sq. ft., or 1 sq. ft. horizontal condensing area for 22.9 sq. ft. hearth area, treating in 24 hr. 961.8 lb. ore mixture.

With the 5-hearth Wedge muffle furnace having a hearth area of 1246 sq. ft. and treating 60 tons of charge in 24 hr. there is in operation a gossage tower 8 ft. 4 in. square (=69.4 sq. ft.) and 41 ft. 3 in. high, or 1 sq. ft. horizontal condensing area for 18 sq. ft. hearth area, treating in 24 hr. 1734 lb. ore mixture.

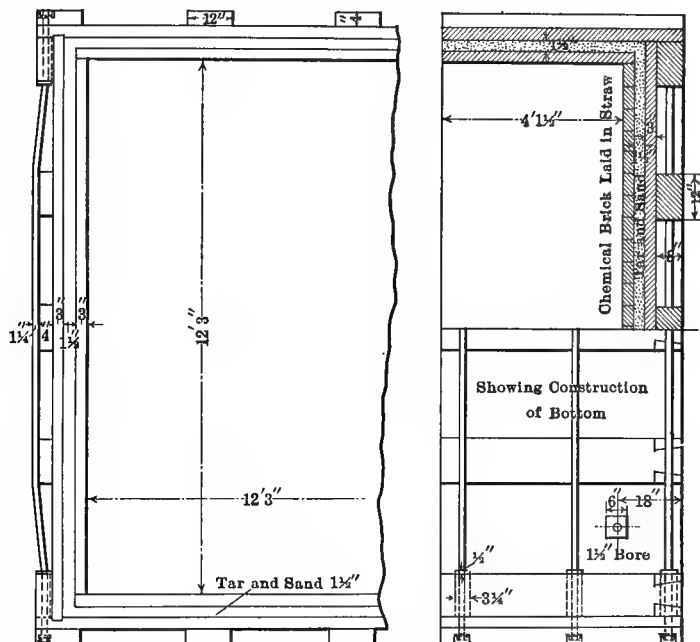
With the Wedge reverberatory furnace the condensing area required is twice that for the muffle furnace.

About 48 cu. ft. of water are required per ton of roasted ore.

**228. Leaching Chloridized Ore by Water and Tower Liquor.**—The leaching vats at present are usually 12 ft. square, 4–5 ft. deep, and hold about 10 tons of charge. They are made of 3-in. planks, well calked with oakum and red lead, and tied by cast-iron corner-pieces and wrought-iron girder-shaped screw bolts. The wood is painted on both sides with tar; in some instances the vats have been lined with lead. The filter-bottom has been constructed in various ways. The simplest is to place on the floor close together  $2 \times 2$ -in. slats beveled at the top and cover them with a filter-bed of small pieces of coke. A better method is to protect the wooden floor with a layer of hard-burnt acid-proof perforated brick and place on this a gravel-filter 6 in. deep, made up of one 3-in. layer of pebbles 1.5 in. in diameter, followed by another of sand 0.75 in. in diameter. Figs. 448–449 show the vat of the Penna. Salt Mfg. Co. of Natrona, Pa. The 3-in. yellow-pine planks used in the construction are well tarred before being put in place. The vat consists of an outer and an inner box separated by a 3-in. layer of sand and soft pitch poured in place. The filter consists of hard-burnt, acid-proof brick laid in straw. Figs. 450–451 represent the spigot for drawing off the solution. In front of a row of tanks are two launders for strong and for weak liquors to be delivered to the clarifying tanks on the next lower level.

The English mode of operating is to dump the ore hot ( $200^\circ \text{C.}$ ) into the vat and then fill the vat with weak wash liquor. This remains in contact with the

ore for about 2 hr., becomes heated, and, dissolving most of the  $\text{CuCl}_2$ , becomes strong ( $8^\circ \text{ Bé.}$ ), so that it can be drawn into the clarifying and thence into the precipitating vats. When withdrawn, the ore is washed with hot water, producing weak liquor, which is stored and serves as first wash-water for another tank. The water-leaches carry at least 75 per cent. of the Cu and 95 per cent. of the Ag. The Cu extracted is purer than that recovered by means of the tower liquor with which the ore-vat is now filled, because this liquor may contain As, Sb, Bi, Pb, etc. The ore used to require as many as six treatments with tower liquor to extract an additional 20 per cent. of Cu.<sup>1</sup> The leaching is not continu-



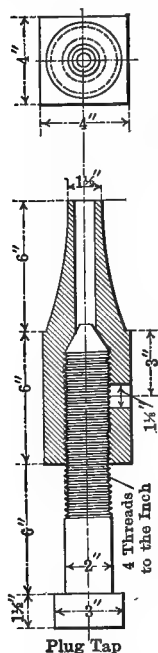
FIGS. 448-449.—Leaching vat, paved with acid-proof brick laid in straw.

ous; the different washes are allowed to remain in contact with the ore for given periods which are determined in part to avoid prolonging the whole treatment beyond 48 hr.

At Oker, Germany, part of the mother liquor from the precipitation of the Cu is used as first solvent after having been heated to 40° C. This liquor being used over and over becomes charged with NaCl, FeCl<sub>2</sub> and other chlorides; it weighs 18° Bé., and contains Cu 0.015, Pb trace, FeO 2.14, Fe<sub>2</sub>O<sub>3</sub> 0.15, Al<sub>2</sub>O<sub>3</sub> 0.11, ZnO 0.06, MnO 0.31 (NiCo)O 0.01, CaO 0.12, MgO 0.52, Alk. 2.61, Cl 2.56, H<sub>2</sub>SO<sub>4</sub> 5.89, As and Sb traces, total solids 14.495 per cent. The FeCl<sub>2</sub> has a chloridizing effect upon CuO; the chlorides assist the solution of

<sup>1</sup> With mechanical furnaces more  $\text{CuCl}_2$  is produced than with hand-raked furnaces as long as the temperature remains the same, so that the water-leach may extract as much as 85 per cent. of the Cu.

$\text{AgCl}$ ,  $\text{AuCl}_3$ , and  $\text{Cu}_2\text{Cl}_2$ .<sup>1</sup> The leaching is continuous and is stopped after from 4 to 5 hr., when the solution ceases to show a bluish color. The liquor extracts from 75 to 80 per cent. of the Cu, weighs  $38^\circ$  Bé., and contains: Cu 3.71, Pb 0.01, Ag 0.005, Bi trace,  $(\text{FeAl})_2\text{O}_3$  0.29, ZnO 4.97, MnO 0.58,  $(\text{NiCo})\text{O}$  0.04, CaO trace, MgO 0.27, Alk. 10.60, Cl 12.56,  $\text{SO}_3$  8.95, As and Sb 0.32 per cent. As in time it becomes overcharged with salts, it is concentrated by storing in vats in the open, and the crystallization of salts assisted by introducing brush-wood. The tower liquor which is subsequently used as solvent is run into the ore-vat, and remains there until its dissolving power has been used up, which lasts about 4 hr. The last solvent is boiling dilute  $\text{H}_2\text{SO}_4$  of  $8^\circ$  Bé.; it remains in contact with the ore for 48 hr. The time for treatment of a charge is about three and one-half days.



FIGS. 450-451.  
—Spigot of Leaching vat.

**229. Clarifying of Copper Liquor.**—The rich copper liquor from the leaching tanks, above  $18^\circ$  Bé. is likely to be cloudy from fine ore,  $\text{PbSO}_4$ , etc. The  $\text{PbSO}_4$  has been found to carry down considerable Au, assaying as much as 5 oz. per ton. The liquor is run into tarred wooden settling tanks, usually 12 ft. square and 6 ft. deep, which have a discharge through a perforated wooden block,  $6 \times 6$  in., placed in the side near the bottom. The number of settling tanks is the same as that of the leaching tanks. Settling takes several hours. In front of a row of tanks is a single launder to receive the clarified liquor.

**230. Precipitation of Copper by Iron.**—A precipitating vat, made of wood and tarred, is 12 ft. square and 6 ft. deep. It has a false bottom of slats 2 ft. above the true bottom, to furnish a support for the iron, and a space for the collection of the cement copper; it is provided with a pipe for heating the liquor by means of live steam, and has a discharge for liquor through a 6-in. wooden block closed by means of a plug. There are half as many precipitating tanks as there are leaching tanks. Each tank is filled loosely with scrap iron, the copper liquor is run in, and the steam turned on to bring it to a boil. Tanks are kept covered with boards to diminish the loss of heat and to retard the formation of oxychlorides, which increase the consumption of Fe. Precipitation may last only 12 hr., but usually takes a day and even longer; it is finished if a bright iron rod does not become tarnished with Cu. When this is the case, the mother liquor is run off through settling tanks, sometimes also through a horse-hair filter, to settle and catch particles of float copper. For the sake of safety the liquors from a row of vats are passed through auxiliary precipitating tanks placed in series; in the overflow of the last is suspended a bright iron rod.

<sup>1</sup> As the presence of  $\text{Cu}_2\text{Cl}_2$  interferes with the precipitation of Ag by KI (Claudet method), it would be necessary to leach first with  $\text{H}_2\text{O}$  and then with mother liquor, if the Ag was to be thus recovered.

There is consumed 1 lb. Fe for 1 lb. Cu, the low consumption being due to the  $\text{Cu}_2\text{Cl}_2$  present. With rich solutions, a clean-up is made once a week; with poor solutions once a month. In both cases the mud is passed over 8-mesh copper screens to remove particles of Fe.

**231. Washing and Refining of Cement Copper.**—The cement copper is transferred from the precipitating tanks to washing-vats, where it is freed from all chloride liquor. Careful washing is essential, as in the subsequent smelting, any Cl would cause a considerable loss of Cu by volatilization. Analyses of cement copper are given in Table 113.

TABLE 113.—ANALYSES OF CEMENT COPPER

	England	Oker, Germany	Hemixen, Belgium	Washed	Natrona, Pa.
Cu.....	72.50	77.45	75.07	95.93	90
Pb.....	2.60	0.63	.....	0.05	.....
Ag.....	0.046	0.10	.....	.....	35 oz.
Bi.....	.....	0.006	.....	.....	Au 0.15 oz.
As.....	0.306	0.04	.....	0.14	.....
Sb.....	.....	0.15	.....	0.35	.....
$\text{Fe}_2\text{O}_3$ .....	4.41	6.72	.....	.....	.....
FeO.....	.....	.....	5.80	2.55 Fe	.....
$\text{Al}_2\text{O}_3$ .....	.....	0.99	2.36	.....	.....
Zn.....	.....	1.02	.....	.....	.....
Mn.....	.....	0.02	0.99	.....	.....
NiCo.....	.....	0.03	.....	0.17	.....
CaO.....	.....	0.10	1.28	0.10	.....
$\text{MgO} + \text{Alk}$ .....	.....	2.71	.....	.....	.....
NaCl.....	.....	.....	0.55	.....	.....
$\text{Na}_2\text{SO}_4$ .....	.....	.....	2.04	.....	.....
$\text{SO}_3$ .....	.....	4.58	.....	0.16	.....
Cl.....	.....	1.19	.....	0.21	.....
Insol. and Loss.....	.....	0.61	4.10	.....	.....
$\text{H}_2\text{O}$ .....	.....	3.654	8.00	.....	.....
Reference	Lunge	Bräuning	Egleston	Stahl, Dissertation, 1886	Clemmer

The washed cement copper is partly dried, compressed, and bagged if it is to be shipped. If it is to be treated at the leaching plant, it is charged more or less moist (8–10 per. cent  $\text{H}_2\text{O}$ ) into a reverberatory furnace either by itself or with the addition of pure white metal, and smelted for blister copper; if it is not sufficiently pure for this purpose, it is added to a matte charge.

**232. Disposition of Residue from Leaching, and of Waste Liquor.**—The residue of the leaching vat is a rich iron ore with  $90 \pm$  per cent.  $\text{Fe}_2\text{O}_3$ , usually low in P and S if it has been well washed. It goes by the name of Purple Ore or Blue Billy. It is removed from the vats by shoveling onto a slightly inclined platform back of the leaching vats, *i.e.*, on the side opposite the clarifying tanks. The platform has discharge-openings through which the ore is transferred into cars after the water has been drained off. Table 114 gives a few analyses.

TABLE 114.—ANALYSES OF PURPLE ORE

	England		Oker, Germany
	Lunge	Lunge	Bräuning
Fe <sub>2</sub> O <sub>3</sub> .....	90.61	95.10	79
Al <sub>2</sub> O <sub>3</sub> .....			3
Cu.....	0.15	0.18	0.3-0.8
S.....	0.08	0.07	
P.....			
PbSO <sub>4</sub> .....	1.46	1.29	
CaSO <sub>4</sub> .....	0.37	0.49	
CaO.....			2.5
MgO+alk.....			1.0
Na <sub>2</sub> SO <sub>4</sub> .....	0.37	0.29	
NaCl.....	0.28		
H <sub>2</sub> SO <sub>4</sub> .....			5.5
Insoluble.....	6.30	2.13	6
Reference	Lunge	Lunge	Bräuning

Purple ore is used as a flux for siliceous lead ores, as a fettling for puddling furnaces, or as an iron ore for blast furnaces. In the last case<sup>1</sup> it is usually first converted into lump form by briquetting and sintering (Gröndall process), by nodulizing, or by mixing with fuel and agglomerating in a Dwight-Lloyd machine whereby the S-content is reduced to traces. The disposition of waste liquor has to be considered in the location of a plant, as the pollution of rivers may cause serious inconveniences. Attempts have been made to recover the Na<sub>2</sub>SO<sub>4</sub>, but they have not been successful (Lunge).

**233. Precipitation of Copper Independently of Silver and Gold.**<sup>2</sup>—Several processes have been devised for the separate recovery of the small amounts of Ag and Au present in the CuCl<sub>2</sub>-solution by precipitating with suitable reagents. Since the perfection of the electrolytic refining of copper, which has reduced the cost to \$4 or \$5 per ton of cathode copper, these processes have lost their former importance.

(1) **THE CLAUDET PROCESS.**—This process is in use in many European plants, but has been given up in this country, as the precipitation was found to be incomplete, leaving, according to Clemmer, 5 oz. Ag. per ton in the copper, and expensive when compared with the price received by the electrolytic refiner who pays for 95+ per cent. of the silver-content.

The process consists of precipitating Ag (Au) by ZnI<sub>2</sub> as AgI, and decomposing the separated precipitate with Zn and HCl whereby the ZnI<sub>2</sub> is regenerated. The Ag-content in the clarified copper liquor from the water-leaches in the English method of leaching, or from the final liquor-wash in the Oker method, is determined, the solution drawn off into a precipitating vat, and diluted with 10 per cent. H<sub>2</sub>O containing an excess of ZnI<sub>2</sub> over that required for the Ag, as some Pb is precipitated as PbI<sub>2</sub>. The dilution causes some PbSO<sub>4</sub> and Cu<sub>2</sub>Cl<sub>2</sub> to separate. The presence of Cu<sub>2</sub>Cl<sub>2</sub> interferes with the complete precipitation of

<sup>1</sup> Hofman, "General Metallurgy," 1913, p. 629, 644.

<sup>2</sup> Stahl, *Berg. Hüttenm. Z.*, 1892, 11, 443.



the Ag. The  $\text{AgI}_2$  settles in about 48 hr.; this time has been reduced to 24 hr. at Oker by the addition of a coagulant of glue (60 g. glue + 10 liters  $\text{H}_2\text{O}$ ) and tannin (30–40 liters) obtained by boiling white-oak bark). The precipitate consists principally of  $\text{AgI}_2$ ,  $\text{PbI}_2$  and  $\text{PbSO}_4$ . It is removed from the vat when a sufficient amount has accumulated, washed, and treated with Zn and HCl. The loss in I is made good by addition of KI. Metallic sponge obtained from its decomposition contained Ag 5.95, Au 0.06, Pb 62.28, Cu. 0.60, ZnO 15.46,  $\text{Fe}_2\text{O}_3$  1.50, CaO 1.10,  $\text{SO}_3$  7.68, Insol. 1.75 per cent. (Lunge).

(2) THE MAYER PROCESS.—Here Ag is precipitated with NaI, and the AgI treated with  $\text{Na}_2\text{S}$ , forming  $\text{Ag}_2\text{S}$ , and NaI. The precipitate at Åtvidaberg contained 10.5 per cent. Ag, that of Königshütte 25.30 per cent.

(3) THE GIBBS PROCESS.—By fractional precipitation with  $\text{H}_2\text{S}$ , nearly all the Ag is thrown down as  $\text{Ag}_2\text{S}$  with about 6 per cent. of the Cu, furnishing a black slime assaying about 200 oz. Ag per ton; the Cu, precipitated later with Fe, assays about 3 oz. Ag per ton.

(4) THE SNELUS PROCESS.—Iron sponge is blown into the solution to precipitate about 19 per cent. of the Cu, which carries down about 80 per cent. of the Ag.

(5) THE JARDINE AND CHADWICK PROCESS.—Dilution of the Cu-liquor is to cause falling out of  $\text{AgCl}$ , and addition of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$  to form  $\text{PbSO}_4$ , which quickly carries down most of the  $\text{AgCl}$ .

**234. Results and Cost.**—The yield in Cu is from 95 to 98 per cent.; that of Ag (Au) is about 75 per cent. with ores assaying from 0.75 to 1.2 oz. Ag and 0.02 oz. Au per ton. The cost of working a ton of burnt Spanish pyrite (in 1899), at Natrona, Pa., with a plant treating 200 tons charge per day with hand-rabbled muffle-furnaces<sup>1</sup> was as follows: Labor, 80 men at \$1.50–2.50, \$134.75; unloading cinder and salt, and loading purple ore, \$35; 21 tons of salt at \$3, \$63; pyrite fines, \$7; 20 tons of coal at \$1, \$20; 5.5 tons of iron scrap at \$7, \$38.50; repairs, depreciations, management, etc., \$40; total \$338.25, or \$1.87 per ton burnt pyrite and \$1.69 per ton mixture. As the 14 furnaces of the plant require 28 men at \$1.75=\$49, the cost of treatment with a mechanical furnace ought to be considerably lower; the amount of salt required ought also to be reduced on account of the more uniform stirring.

The cost of treatment at present (including grinding, furnacing, leaching, precipitating with recovery of a portion of the gold, silver, and lead values), using an eight-hearth furnace (Fig. 447) and recovering 47 lb. copper is, according to the best European practice, substituting American prices for labor: Labor in process \$0.67; labor in repairs \$0.11; materials in process \$0.70; materials in repairs \$0.20; total \$1.68. The cost of materials used in the process (70 cents) is made up as follows: fuel for boilers 8 cents; fuel for furnacing 8 cents (4 per cent. coal<sup>2</sup> on burnt pyrite at \$2.16 per ton); salt 38 cents; iron 10 cents; miscellaneous 6 cents. The cost of furnacing alone is \$0.25 (labor 13 cents, fuel 8 cents, repairs 4 cents).

<sup>1</sup> Clemmer, *Min. Ind.*, 1899, VIII, 202.

<sup>2</sup> Some European plants use only 2 per cent. coal.

## B. LEACHING COPPER MATTE

**235. Leaching of Copper Matte in General.**—Wet treatment of copper matte need to be considered only when this carries precious metals; if this is not the case, the matte is usually brought forward to metal by some smelting process. Lixiviation of copper matte was more common formerly than it is at present, when matte is being more and more brought forward to metallic copper to be refined electrolytically, as not only are Ag and Au recovered, but a high-grade metallic copper is produced instead of blue vitriol, for which the return is likely to be unsatisfactory.

The processes used for leaching copper matte are of two kinds. In both the matte is given a preliminary roast. In the first, the Ag is converted to AgCl (Augustin process) or  $\text{Ag}_2\text{SO}_4$  (Ziervogel process), dissolved, and the CuO later reduced to metal; in the second, the Ag remains intact while the CuO is dissolved by  $\text{H}_2\text{SO}_4$ , and either sold as blue vitriol (Freiberg, Hofmann processes) or precipitated as  $\text{Cu}_2\text{Cl}_2$  and then reduced to metal (Hunt and Douglas process, No. II).

**236. The Augustin Process.**<sup>1</sup>—The process has been used for ore, matte, speise, and metallic copper (§ 242). The leading steps in the process with copper matte are: oxidizing roast to produce CuO and  $\text{Ag}_2\text{SO}_4$ ; chloridizing roast to convert  $\text{Ag}_2\text{SO}_4$  into AgCl; solution of AgCl in hot brine; precipitation of Ag by means of Cu; recovery of Cu by means of Fe. The process is obsolete. The principal reasons for this are: the small dissolving power of brine<sup>2</sup> for AgCl necessitating heating, storing, and handling of large volumes of liquor; the imperfect extraction of Ag, especially in the presence of As, Sb, and Zn; the volatilization of  $\text{AuCl}_3$  and its insolubility in brine. The process was used at Mansfeld, Prussia, from 1840 to 1849;<sup>3</sup> Freiberg, Saxony, from 1848–1862;<sup>4</sup> at Black Hawk, Colo.,<sup>5</sup> where it served to increase the yield in Ag from the Ziervogel process (§ 237); at Kosaka, Japan<sup>6</sup> in conjunction with the Paterna process; and other places.

**237. The Ziervogel Process in General.**<sup>7</sup>—This process was invented in

<sup>1</sup> A. Grützner, "Die Augustin'sche Silberextraction in ihrer Anwendung auf Hüttenproducte und Erze," Vieweg, Brunswick, 1851.

Kerl-Crookes-Röhrig, "Practical Treatise on Metallurgy," Longmans, Green & Co., London, 1868, I, 368.

Rivot, L. E., "Traité de Métallurgie," Dunod, Paris, 1871, I, 405.

Howe, "Production Gold and Silver in the U. S., 1883, p. 764.

Balling, C. A. M., "Metallhüttenkunde," Springer, Berlin, 1885, p. 355.

<sup>2</sup> Hahn, *Tr. A. I. M. E.*, 1873–74, II, 99; *Eng. Min. J.*, 1898, LXV, 434.

<sup>3</sup> Grützner, *loc. cit.*

<sup>4</sup> Kerl-Crookes-Röhrig, *loc. cit.*

<sup>5</sup> Egleston, *Tr. A. I. M. E.*, 1875–76, IV, 295.

<sup>6</sup> Kmabara, *School Min. Quart.*, 1893–94, XV, 355.

<sup>7</sup> Steinbeck, *Zt. Berg. Hütten. Salin. Wesen i. P.*, 1863, XI, 95.

Rivot, L. E., "Traité de Métallurgie," 1871, I, 425.

Howe, "Production Gold and Silver in the U. S., 1883, p. 753.

Bradford, *Tr. A. I. M. E.*, 1903, XXXIII, 50.

At Mansfeld: Leuschner, *Zt. Berg. Hütten. Salin. Wesen i. P.*, 1869, XVII, 135; *Berg.*

1840, introduced at Mansfeld in 1844, and is carried on there at present. Pulverized silver-bearing high-grade copper matte is subjected to a sulphatizing roast to form  $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Ag}_2\text{SO}_4$ ; the  $\text{Ag}_2\text{SO}_4$  is dissolved with hot  $\text{H}_2\text{O}$  acidulated with  $\text{H}_2\text{SO}_4$ , and precipitated from its solution with granulated or sheet copper. The resulting mother liquor is used again as solvent for  $\text{Ag}_2\text{SO}_4$  and its Cu recovered at intervals by means of Fe. The leached  $\text{CuO}$ , containing some  $\text{Fe}_2\text{O}_3$ , and any precipitated Cu are smelted in a reverberatory furnace for blister copper. Besides in Mansfeld, the process has been (is?) in use at Swansea, Wales, and Argo, Colo. (closed in 1909).

The process is suited only for a reverberatory furnace or converter matte which runs high in Cu, low in Ag, and is pretty free from impurities, such as Pb, As, Sb, Bi. The Cu must be present as  $\text{Cu}_2\text{S}$ ; 0.06 per cent. is the limit for metallic Cu if the sulphatization of the Ag is to be satisfactory. The Cu-content must be high in order to furnish the necessary  $\text{SO}_3$  from the decomposition of  $\text{CuSO}_4$  for sulphatizing  $\text{Ag}_2\text{S}$ , which in its turn must be rightly apportioned to the Cu-content. The compounds  $\text{PbS}$  and  $\text{Sb}_2\text{S}_3$  cause sintering; As and Sb form insoluble  $\text{Ag}_3\text{AsO}_4$  and  $\text{AgSbO}_3$ , and Bi<sup>1</sup> an insoluble  $\text{Bi}_2(\text{SO}_4)_3 \cdot x\text{Ag}_2\text{SO}_4$ . The matte treated at Mansfeld up to 1874 contained 64–65 per cent. Cu; since then 74–75 per cent. has been made the standard, as the results of a series of tests carried on between 1869 and 1871 had shown that the higher tenor gave a better yield in Ag as well as a higher grade of Cu. The leading components of the matte are: Cu 74, Ag 0.4, Pb 0.6–0.8, Fe 1.2–2.0, Ni 0.4, Co 0.1, As 0.01, Sb none, S 19–20, metallic Cu 0.03–0.05 per cent. The white and the pimple metal treated at Argo assayed Cu 60 per cent., Ag 750 oz., Au 10 oz. per ton, and Cu 77 per cent., Ag 90 oz., Au 0.2 oz. per ton.

The following discussion is confined to Mansfeld; the Colorado plant, which was stopped in 1909 and will not be taken up again, has been described by Pearce;<sup>2</sup> details of English practice have not been made public.

### 238. Ziervogel Process at the Gottesbelohnung Works, Mansfeld.

(1) CRUSHING.—The matte with 74–75 per cent. Cu, broken by hand, is pulverized in ball-mills to pass a 16-mesh screen; a Brückner-Sachsenberg mill with 0.5 ton of 4-in. balls pulverizes in 24 hr. 17 tons of matte; a Gruson mill with 0.7 ton of 6-in. balls, 24 tons.

(2) ROASTING.—In roasting,  $\text{FeS}$  is converted into  $\text{Fe}_2\text{O}_3$  passing in part through the stages of  $\text{FeSO}_4$  and  $\text{Fe}_2\text{SO}_6$ ; the behavior of  $\text{Cu}_2\text{S}$  is similar excepting that  $\text{Cu}_2\text{O}$  is formed as long as there is present any  $\text{Cu}_2\text{S}$ , and has to be converted completely into  $\text{CuO}$ . The  $\text{SO}_3$  set free by the decomposition of  $\text{CuSO}_4$  causes  $\text{Ag}_2\text{S}$  and  $\text{Ag}_2$  to be converted in  $\text{Ag}_2\text{SO}_4$  as shown by  $\text{Ag}_2\text{S} + 4\text{SO}_3 =$

*Hüttenm. Z.*, 1869, XXIX, 432; Report of 1881, *op. cit.*, 1881, XL, 430; Report of 1904, *Metalurgie*, 1904, I, 229; Report of 1907, *op. cit.*, 1908, v, 27. Egleston, *School Min. Quart.*, 1890–91, XII, 207. Private Notes, 1911. Private Communication by R. Franke, 1913.

In Colorado: Egleston, *Tr. A. I. M. E.*, 1876, IV, 276.

Pearce, *op. cit.* 1889–90, XVIII, 55.

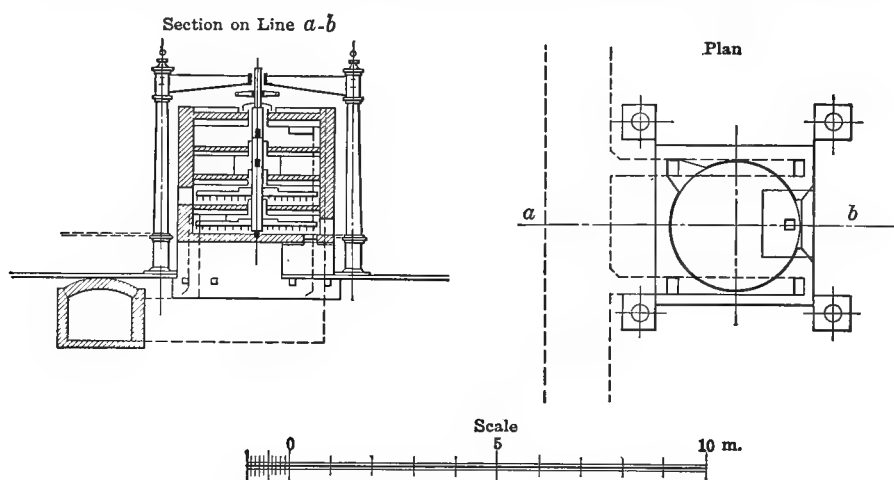
<sup>1</sup> Pearce, *op. cit.*, 1889–90, XVIII, 67.

<sup>2</sup> *Loc. cit.*

$\text{Ag}_2\text{SO}_4 + 4\text{SO}_2$  and  $2\text{Ag} + 2\text{SO}_3 = \text{Ag}_2\text{SO}_4 + \text{SO}_2$ . Sulphatization of Ag, however, is difficult and unsatisfactory.

The roasting operation is divided into the stages of rough-roast and finishing-roast; the latter operation is repeated once with leached matte.

The rough-roast, Figs. 452-453, is carried on in a four-hearth circular mechanical fine-ore kiln, 12 ft. 5 $\frac{5}{8}$  in. in diameter, with central vertical driving shaft, which has two rabbling arms with trailing teeth to each hearth, and is geared from above to make 1.25 r.p.m. The two upper hearths are connected by a flue as well as the two lower. The heat necessary for roasting is furnished by the oxidation of the matte. The furnace is fed by charges, and therefore works intermittently. Each upper hearth receives a charge of 1.4 tons of matte, which is roasted at a temperature of 500-600° C. The charge remains 3 hr. on the upper hearth and is then transferred to the lower, where it roasts

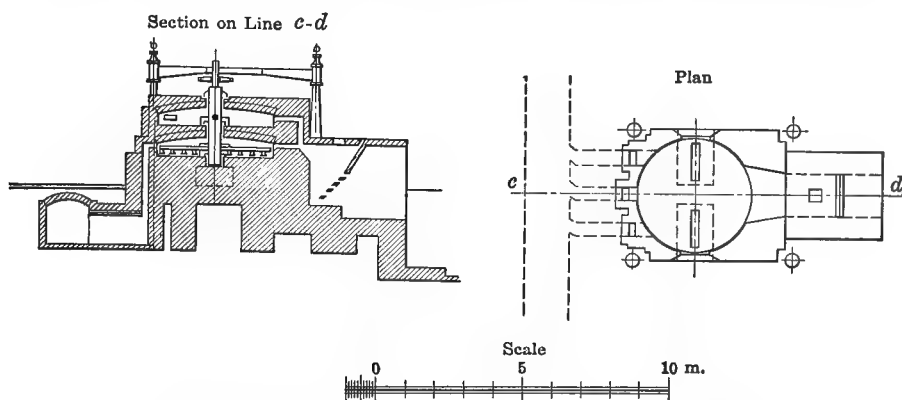


FIGS. 452-453.—Mechanical rough-roasting kiln.

4 hr. 52 min. more. A furnace with its pair of double hearths treats in 24 hr. 14 tons of matte. The rough-roasted matte retains 5 per cent. S, the  $\text{Ag}_2\text{S}$  remains unchanged;  $\text{FeS}$  is converted into  $\text{Fe}_2\text{O}_3$ ; 45 per cent. of the Cu is present as  $\text{Cu}_2\text{O}$ ; the remaining 55 per cent. as  $\text{Cu}_2\text{S}$ ,  $\text{CuSO}_4$ , and  $\text{CuO}$ . If the S- or the  $\text{Cu}_2\text{O}$ -content varies much from the above figures, the extraction of Ag becomes unsatisfactory. The roasted ore goes to the cooling floor, where it remains 8 hr., and is then reground in the ball-mill. The life of the furnace is from 8 to 12 years.

The finishing-roast is carried on in a two-hearth furnace, Figs. 454-455, of similar general construction as the rough-roasting kiln and of the same dimensions; it is, however, fired with producer gas. The step-grate of the Zahn producer is 1 ft. 7 $\frac{3}{4}$  in. by 5 ft. 10 $\frac{3}{4}$  in., the height 3 ft. 11 $\frac{1}{4}$  in. and 4 ft. 7 $\frac{1}{8}$  in., the flue 4 ft. long; the flame is split to reach the upper and lower hearths; the roaster-gases pass downward into an underground main. The driving shaft

makes 1.75 r.p.m. The temperature is  $850^{\circ}\text{C}$ . A charge of 1.75 tons of rough-roasted matte is dropped onto the upper hearth, remains there 1.75 hr., whereby the 45 per cent.  $\text{Cu}_2\text{O}$  are reduced to 12 per cent., and then transferred to the lower hearth where the remaining  $\text{Cu}_2\text{O}$  is oxidized to  $\text{CuO}$  in 3 hr., and the  $\text{Ag}_2\text{S}$  converted into  $\text{Ag}_2\text{SO}_4$ . The side doors are kept partly open to allow the air to have free access. The sulphatized matte goes to the cooling floor, where it cools in 8 hr. to  $70\text{--}80^{\circ}\text{C}$ ., to be sifted at this temperature into the leaching vats. The furnace treats in 24 hr. 14 tons of rough-roasted matte and



FIGS. 454-455.—Mechanical sulphatizing reverberatory furnace.

consumes 1.7 tons of bituminous coal. After every removal of a charge the path of the rabble-arms is reversed. It is essential to have uniformly strong oxidizing conditions and a correct temperature for the control of the formation of  $\text{Ag}_2\text{SO}_4$ . An important factor is the amount of  $\text{Cu}_2\text{O}$  present. At  $850^{\circ}\text{C}$ . an excess of  $\text{Cu}_2\text{O}$  over 45 per cent. begins to act upon  $\text{Cu}_2\text{S}$  setting free  $\text{Cu}$ ; further  $\text{Cu} + \text{Ag}_2\text{S}$  gives  $2\text{Ag} + \text{Cu}_2\text{S}$ , and  $\text{Ag}_2$  is difficult to sulphatize; again  $\text{Cu}_2\text{O}$  decomposes  $\text{Ag}_2\text{S}$  in the dry way<sup>1</sup> as well as in the wet way:  $\text{Cu}_2\text{O} + \text{Ag}_2\text{SO}_4 = \text{CuSO}_4 + \text{CuO} + 2\text{Ag}$  (spangle-reaction). If the temperature is too low,  $\text{CuSO}_4$  remains undecomposed,  $\text{Ag}_2\text{S}$  is imperfectly sulphatized, and the ore upon leaching begins to cake; if it is too high  $\text{Ag}_2\text{SO}_4$  is decomposed.<sup>2</sup>

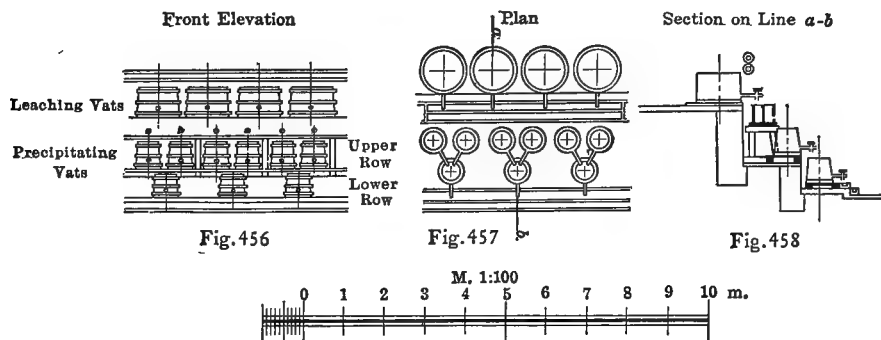
At Argo<sup>3</sup> 2 per cent. of  $\text{NaHSO}_4$  used to be added to the finishing-roast to assist in the sulphatization of the  $\text{Ag}$ .

<sup>1</sup> Plattner, "Röstprocesse," p. 141.

<sup>2</sup> An interesting side-issue at these works is the utilization of the  $\text{SO}_3$  set free in the finishing roast. The gases are passed through a long flue charged with the dust, collected in the wet condensation of the blast-furnace gases, which contains  $\text{ZnO}$ , some  $\text{ZnSO}_4$ ,  $\text{PbO}$ ,  $\text{PbSO}_4$ , etc., and readily absorbs  $\text{SO}_3$ . The dust is worked up at the rate of 2.4 tons per day by treating with  $\text{H}_2\text{O}$  and some  $\text{H}_2\text{SO}_4$  in an upright stationary cylindrical vat with mechanical stirrer to which some blue powder is added to precipitate all the  $\text{Cu}$  and  $\text{Ag}$ . The leached mud is filter-pressed, and the filtrate of  $32^{\circ}\text{Bé}$ . evaporated in a Patzbug vacuum pan furnishing granular  $\text{ZnSO}_4$ -crystals used in the manufacture of lithopone; the residue is sold to lead works.

<sup>3</sup> Eng. Min. J., 1890, XLIX, 203.

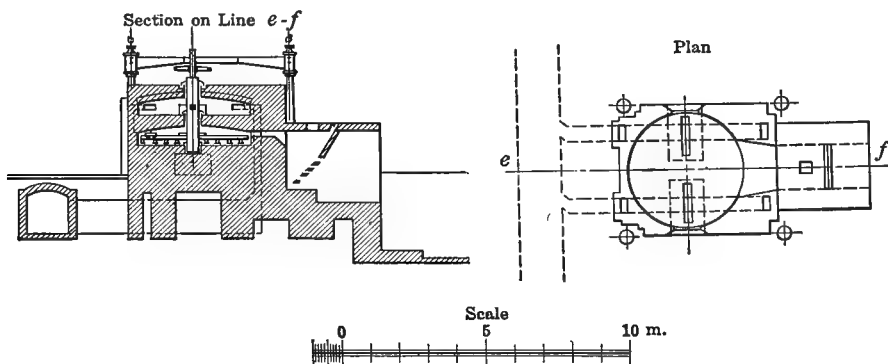
The progress of the roast is followed by the appearances of the solution obtained in leaching samples with  $H_2O$ . At first, the solution will be greenish from  $FeSO_4$ , later blue from  $CuSO_4$ ;  $NaCl$  will give a slight curdy precipitate of  $AgCl$ , and its amount will increase slowly as the formation of  $Ag_2SO_4$  progresses; bright spangles of  $Ag$  separating from the solution show that  $Cu_2O$



FIGS. 456-458.—Leaching and precipitating division.

is decomposing  $Ag_2SO_4$ . The roast is finished when the blue color caused by  $CuSO_4$  has nearly disappeared, the spangle reaction has ceased, and  $NaCl$  gives a heavy precipitate of  $AgCl$ .

(3) LEACHING.—The sulphatized matte is leached in wooden vats with false bottoms and duck filters, Figs. 456-458. A vat is 40 in. in diameter, 31.5 and 35.4 in. deep, receives a sifted charge of 0.7 ton, is leached in 4 hr. with hot



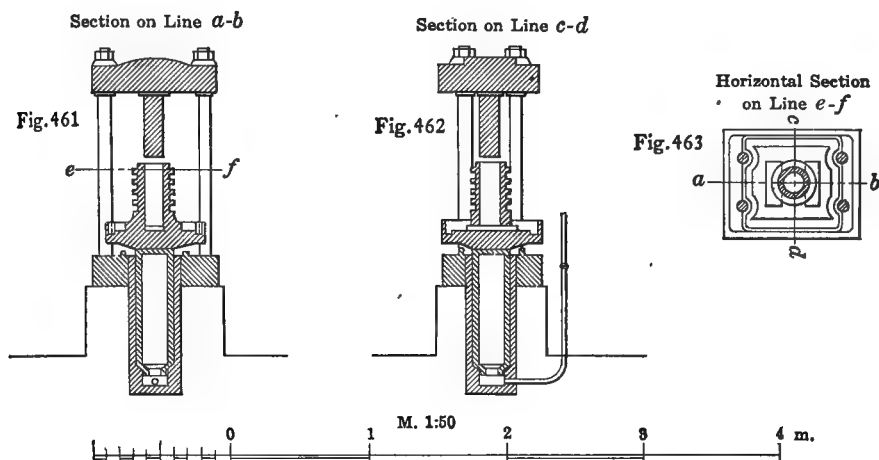
FIGS. 459-461.—Auxiliary mechanical sulphatizing reverberatory roasting furnace.

$H_2O$  ( $70-80^\circ C.$ ) and then with hot desilverized liquor that has been acidulated. The silver has been extracted when a bright  $Cu$  plate is not tarnished and  $NaCl$  ceases to produce any turbidity. For 1 kg.  $Ag$  recovered there is used 1 liter  $H_2SO_4$  of  $35^\circ B\acute{e}$ . The leached residue retains 0.025-0.035 per cent. (7-10 oz. per ton)  $Ag$ . An analysis<sup>1</sup> of the residue showed  $Cu$  73.93,  $Ag$  0.0268,  $Pb$

<sup>1</sup> Die Mansfeld'sche Kupferschiefer Bauende Gewerkschaft," 1907, p. 147.

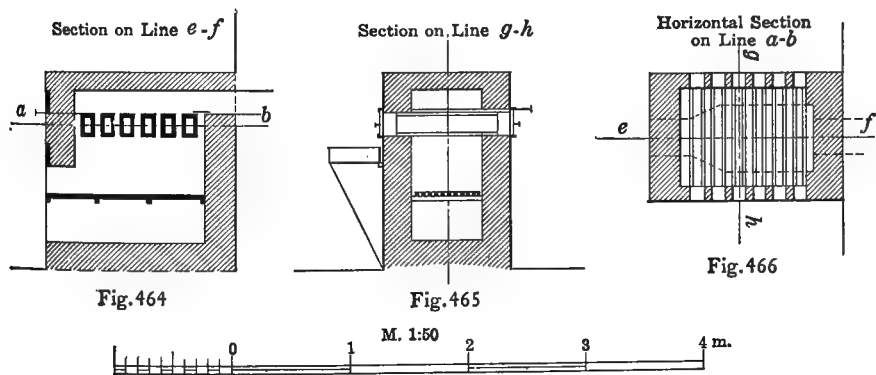
0.557, Ni 0.436, Co 0.140, sulphate-S 0.466, sulphide-S 0.062, total-S 0.528 per cent.

In order to reduce further the Ag-content, the leached residue is roasted again at 650–700° C. in a two-hearth mechanical reverberatory furnace, Figs.



FIGS. 461–463.—Hydraulic press for cement silver.

459–460, similar to the sulphatizing furnace, in which the driving shaft makes  $\frac{1}{2}$  r.p.m. The residue retains enough sulphide-S to effect the desired sulphatization. The furnace is charged with from 3.4 to 3.7 tons of drained residue, remains on the upper hearth 1.75 and on the lower 3 hr., is leached in 0.7-ton charges, in 3 to 4 hr. The final residue now assays Cu 73–74, Ag

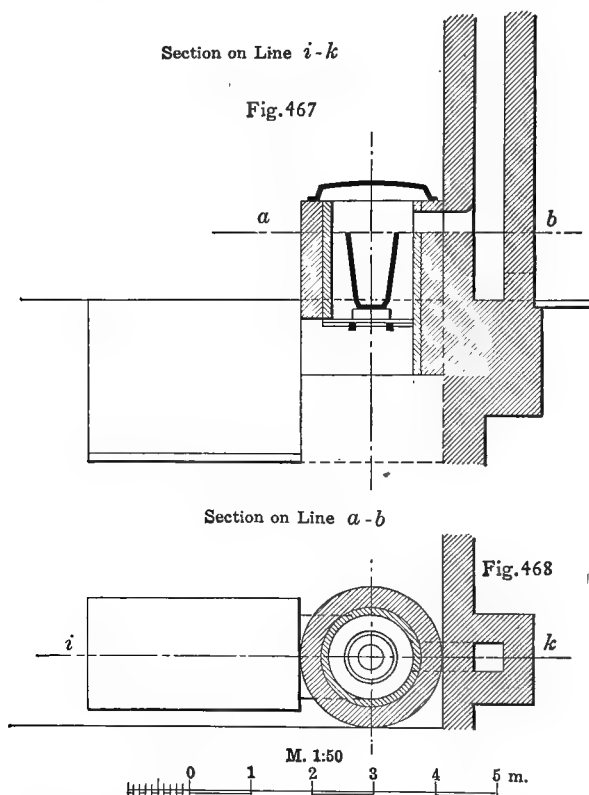


FIGS. 464–466.—Drying and calcining furnace for cement silver.

0.016, (4.6 oz. per ton), Pb 0.5–0.8, Ni 0.4, Fe 1.2–2.0, As 0.015–0.020, S 0.5 per cent. It is smelted and refined in a reverberatory furnace (Table 93).

(4) PRECIPITATING.—The silver liquor, clarified by traveling through a pair of settling and distributing troughs, or by filtering when necessary, is freed

from Ag by percolating through two rows of small (24 in. in diameter, 20 in. deep, with slight taper toward bottom) wooden vessels provided with false bottom and filled with granulated Cu. The upper row of vessels contains corroded granules over which silver liquor has passed for some time. The Cu of the granules has been more or less replaced by Ag, and the bulk of the Ag has been detached by rubbing and then removed. The lower row of vessels contains fresh granules. When the Cu in an upper vessel has been entirely replaced by



FIGS. 467-468.—Crucible-furnace for melting cement silver.

Ag, the vessel is removed, the lower one transferred to the upper shelf, and another vessel filled with fresh granules placed on the lower.

(5) FURTHER TREATMENT OF SILVER.—The cement silver, about 0.996 fine, is washed, compacted in a hydraulic press, Figs. 461-463, into cakes 7.78 in. in diameter, dried and calcined in iron boxes, Figs. 464-466, and melted in a crucible furnace, Figs. 467-468, and cast. The bars contain Ag 99.920-99.950, Cu 0.02-0.04, Pb 0.004-0.008 per cent. In 1906 a ton of white metal (Cu 73-74 per cent.) yielded 56.5 oz. Ag; the extraction was 92 per cent.; the cost of treatment was about \$7 per ton of matte.



**239. The Freiberg Vitriolization Process.**<sup>1</sup>—The aim of the process is to dissolve with hot dilute  $\text{H}_2\text{SO}_4$  the  $\text{CuO}$  from high-grade dead-roasted argentiferous matte and convert it into marketable blue vitriol; the insoluble silver-bearing residue is added to a lead blast-furnace charge. The process is based upon the solubility of  $\text{CuO}$  and the relative insolubility of  $\text{Ag}(\text{Au})$  in dilute  $\text{H}_2\text{SO}_4$ . If dead-roasted copper matte is treated with hot dilute  $\text{H}_2\text{SO}_4$ ,  $\text{CuO}$  and  $\text{ZnO}$  will first go into solution, then follow  $\text{Fe}_2\text{O}_3$ ,  $\text{NiO}$  and  $\text{CoO}$ , and to a very small extent  $\text{Ag}$ . Any  $\text{Cu}_2\text{O}$  present is decomposed,  $\text{Cu}_2\text{O} + \text{H}_2\text{SO}_4 = \text{Cu} + \text{CuSO}_4 + \text{H}_2\text{O}$ . The  $\text{Cu}$  will precipitate some  $\text{Ag}$  that may have been dissolved, but the dead-roast is usually prolonged sufficiently to convert all  $\text{Cu}_2\text{O}$  into  $\text{CuO}$ . The  $\text{PbO}$  present is changed into  $\text{PbSO}_4$ . Arsenates and antimonates will be partly decomposed, the former being more soluble than the latter. The residue will contain  $\text{Ag}(\text{Au})$ ,  $\text{PbSO}_4$  and other insoluble sulphates.

The process was developed at Freiberg, Saxony; it has been replaced there by the vitriolization of metallic  $\text{Cu}$ ; in the United States it is in operation at the Selby Lead Works, San Francisco, Cal., where blue vitriol is produced from matte.

(1) MATTE.—The matte to be suited for the process ought not to contain more than 0.2 per cent.  $\text{Fe}$ , as the  $\text{FeSO}_4$  formed would crystallize with the  $\text{CuSO}_4$  and decrease its market value.

However, Gin<sup>2</sup> has invented a process for the separation of the two sulphates. It is based upon the fact that the solubility of  $\text{CuSO}_4$  is at its maximum at  $100^\circ \text{C}$ . and diminishes very slowly with a rise of temperature, while that of  $\text{FeSO}_4$  reaches its maximum a little below  $100^\circ \text{C}$ . and then falls off very quickly being practically *nil* at  $160^\circ \text{C}$ . If a mixed moderately concentrated (350–400 g.  $\text{CuSO}_4 + \text{aq.} : 1$  liter) solution, kept at nearly boiling temperature, is pumped into a tubular boiler, having an active circulation, and heated there to  $180^\circ \text{C}$ . (=about 200 lb. steam pressure), the  $\text{FeSO}_4$  will separate. The  $\text{CuSO}_4$  liquor with suspended  $\text{FeSO}_4$  crystals is forced from the boiler through a filter-press, with chambers kept hot by steam at 220 lb., to separate the crystals from the liquor. While the process is interesting, it seems more rational to scorify the  $\text{Fe}$  in the reverberatory smelting necessary to obtain a matte rich in  $\text{Cu}$ , than to cut short the dry process and extend the wet with its inherent complications.

An analysis of Freiberg matte by Schertel<sup>3</sup> gave  $\text{Pb}$  4.85,  $\text{Ag}$  0.31,  $\text{Cu}$  73.95,

<sup>1</sup> Kuhlmann, *Zl. Berg. Hütten. Salin. Wesen i. P.*, 1871, XIX, 180; *Berg. Hüttenm. Z.*, 1872, XXXI, 76.

Capacci, *Rev. Un. Min.*, 1881, IX, 276.

Howe, "Production Gold and Silver in the U. S.," 1883, 790.

Doerr, *Min. Ind.*, 1896, V, 225.

Gignoux (Lyon Mill, Dayton, Nev.), *Min. Res. U. S.*, 1882, 297.

Rickard, *Min. Ind.*, 1908, XVII, 588, Selby Lead Works, San Francisco, Cal.

<sup>2</sup> Fifth Internat. Congr. Appl. Chemistry, Berlin, 1903, I, 597; *Eng. Min. J.*, 1903, LXXVI, 358.

<sup>3</sup> Hofman, "Lead," 1898, p. 373.

Bi 0.02, Sb 0.06, As 0.18, Fe 0.13, NiCo 0.21, S 18.98. The matte usually assays Cu 70-75 per cent. Fe < 0.20 per cent.

(2) CRUSHING AND ROASTING.—The matte is stamped dry to pass a 6-mesh sieve, and dead-roasted in a two-hearth hand reverberatory furnace receiving charges of 3520 lb., which pass through it in about 16 hr. The roasted matte retains about 1 per cent. S, is ground in a buhrstone mill, and sifted through an 80-mesh screen; the oversize is returned to the mill.

(3) LEACHING.—The leaching-vats are hard-lead cylindrical vessels, 0.78 in. thick, 5 and 4 ft. in diameter, and 4 ft. high; they have a side discharge near the bottom. A vat is charged with 440 lb.  $\text{H}_2\text{SO}_4$  of  $50^\circ$  Bé. and 880 lb. mother liquor. This solvent is heated with superheated live steam, and 360 lb. roasted matte stirred in in 2 hr. When the solution, lasting 5 hr., is finished, the steam is shut off, the concentrated liquor diluted to  $32^\circ$  Bé., the residue allowed to settle for 1 hr., and the Cu-liquor siphoned into a clarifying vat to remain 1 hr., and thence into wooden crystallizing tanks of about 90 cu. ft. capacity, lined with soft lead, 0.2 in. thick for sides, 0.4 in. for bottom. Here the  $\text{CuSO}_4 + \text{aq.}$  crystallizes out in from 10 to 21 days on suspended lead strips 1 in. wide and 0.2 in. thick, as well as on the sides and the bottoms of the tanks. The mother liquor serves to dilute chamber acid. The bottom and side crystals, imperfectly developed, are likely to retain some insoluble residue; they are redissolved in  $\text{H}_2\text{O}$  and mother liquor from the second crystallization to form a solution of  $32\text{--}34^\circ$  Bé. The crystals of blue vitriol contain Fe 0.05-0.06, Ni 0.006, Zn 0.003, Pb 0.004 per cent. The residue in the solution vat is removed, settled, drawn off into a conical lead-lined wooden box, treated with  $\text{H}_2\text{SO}_4$  and steam, filtered, washed, and then added to the charge of a lead blast-furnace; it forms 15 per cent. of the weight of the matte and assays, Ag 1.3-2 per cent., Cu 3-8, Pb 40-50 per cent. Mother liquor becoming too heavily charged with  $\text{FeSO}_4$  to furnish clean blue vitriol is treated with Fe to precipitate cement Cu.

Of the Cu charged there is recovered 96.6 per cent. in blue vitriol, 0.9 in residue, 0.1 in flue-dust, 0.15 in drosses, 1.3 in cement copper, 0.15 in the precipitating iron, total 99.2 per cent.

**240. The Hofmann Vitriolization Process.**<sup>1</sup>—The process developed and put into operation at the works of the Kansas City Smelting and Refining Co., Argentine, Kan. (now dismantled), resembles in its general features the Freiberg vitriolization in that CuO is extracted from roasted ore by means of  $\text{H}_2\text{SO}_4$  and crystallized as  $\text{CuSO}_4 + \text{aq.}$ ; it differs from it in that any Fe present is precipitated as  $\text{Fe}_2\text{O}_3$ , and this permits the use of matte rich in Fe as raw material. The process is of sufficient importance to warrant a full discussion.

(1) THE MATTE.—The raw material is the leady copper matte usually produced by the concentration in the blast-furnace of the matte formed in

<sup>1</sup> Hofmann, O., *Min. Ind.*, 1899, VIII, 189; 1900, IX, 222; 1901, X, 230; "Hydrometallurgy of Silver," McGraw-Hill Book Co., New York, 1907, p. 259.

Hesse, "Works at Predazzo," *Metallurgie*, 1909, VI, 580, drawings.

smelting copper-bearing lead ores; it contains Cu 36, Pb 13, Fe, etc., 30, S 21 per cent.

(2) ROASTING.—The matte is crushed in a rock breaker, and pulverized in a 100-ton Krupp ball-mill to pass a 50-mesh screen. The pulp is roasted in a

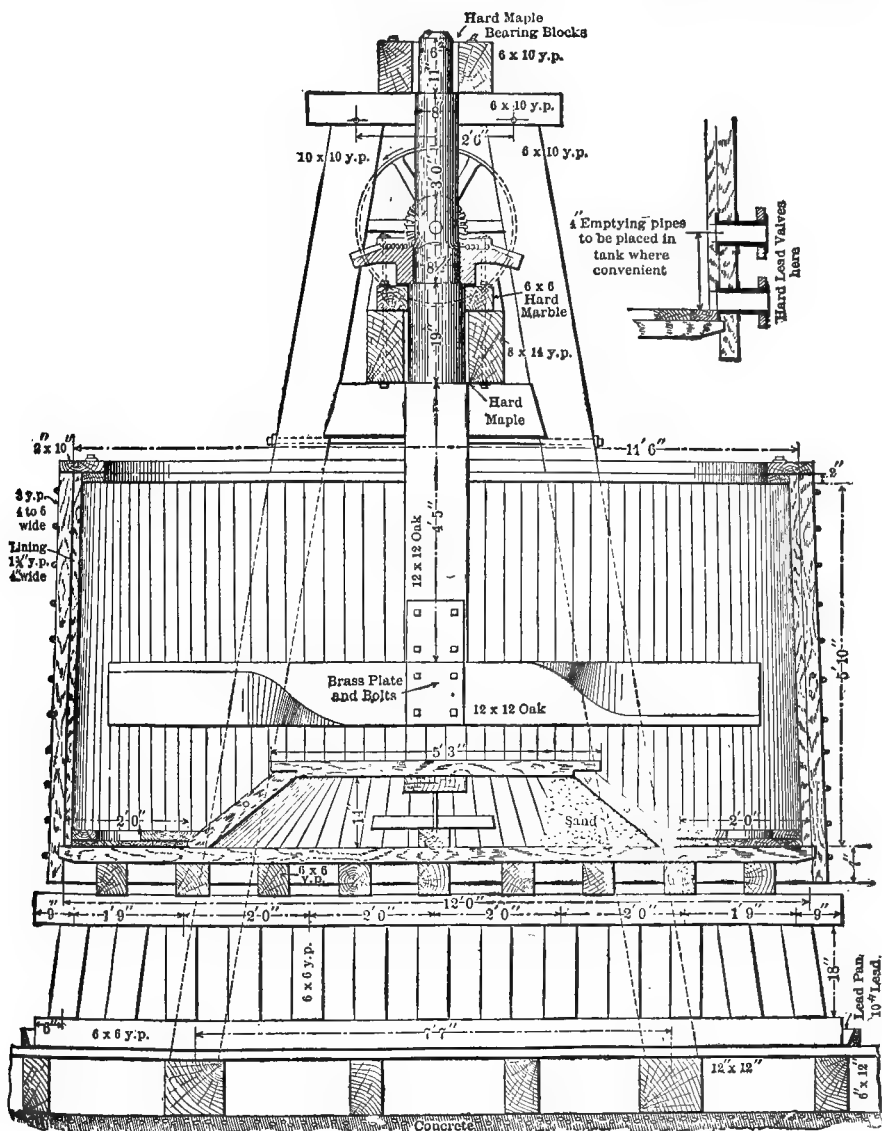


FIG. 469.—Hofmann lixiviation vat with mechanical stirrer.

two-hearth Pearce turret furnace, Figs. 151-152, 40 ft. in diameter, having three fire-places for the lower and two for the upper hearth. The roast is carried on in such a way as to convert all the  $\text{FeS}$  into  $\text{Fe}_2\text{O}_3$  and about 75 per

cent. of the Cu into CuO. This is accomplished by keeping the temperature low on the upper hearth, and at a cherry red ( $700-750^{\circ}$  C.) on the lower.

The roasting matte at first looks a bright red from the oxidation of the sulphide and becomes darker later on. It is then necessary to urge the fire, but there is danger of overheating, which causes the yield in soluble Cu to fall off. As the formation of some lumps cannot be avoided, the roasted matte is passed again through a Krupp ball-mill with a 50-mesh screen.

(3) LEACHING.—This is carried on in the stationary tank, 12 ft. in diameter and 6 ft. high, with mechanical stirrer, shown in Fig. 469.<sup>1</sup> The tank is of wood, has a central cone-shaped projection fastened to the bottom, which forces the matte toward the periphery, where it is held in suspension by the swiftly moving solvent.<sup>2</sup> The interior of the projection is filled with sand. The stirrer, a suspended vertical shaft with two horizontal propeller-shaped arms, is driven by gearing. The rim of the tank has a wooden ring to prevent splashing of the liquor. In the side near the bottom are two discharge pipes of which usually the lower one only is used. The tank is carried by a framework standing in a lead pan, intended to catch any leakage, which rests on a floor carried by sills.

In leaching, the tank is filled two-thirds with  $H_2O$ , the stirrer started, 3 per cent.  $H_2SO_4$  added, and live steam introduced. The matte is fed in gradually from a dump-car with covered discharge provided with a slot; at the same time  $H_2SO_4$  is run in at a rate to maintain the original standard of 3 per cent. free  $H_2SO_4$  in the liquor. Working in this way with little free acid causes little  $Fe_2O_3$  to be dissolved, the solution showing only 0.7–1.0 per cent. Fe. When the liquor measures  $20-22^{\circ}$  Bé., the flow of acid is shut off, and matte added in small amounts at a time until the free acid has been neutralized.

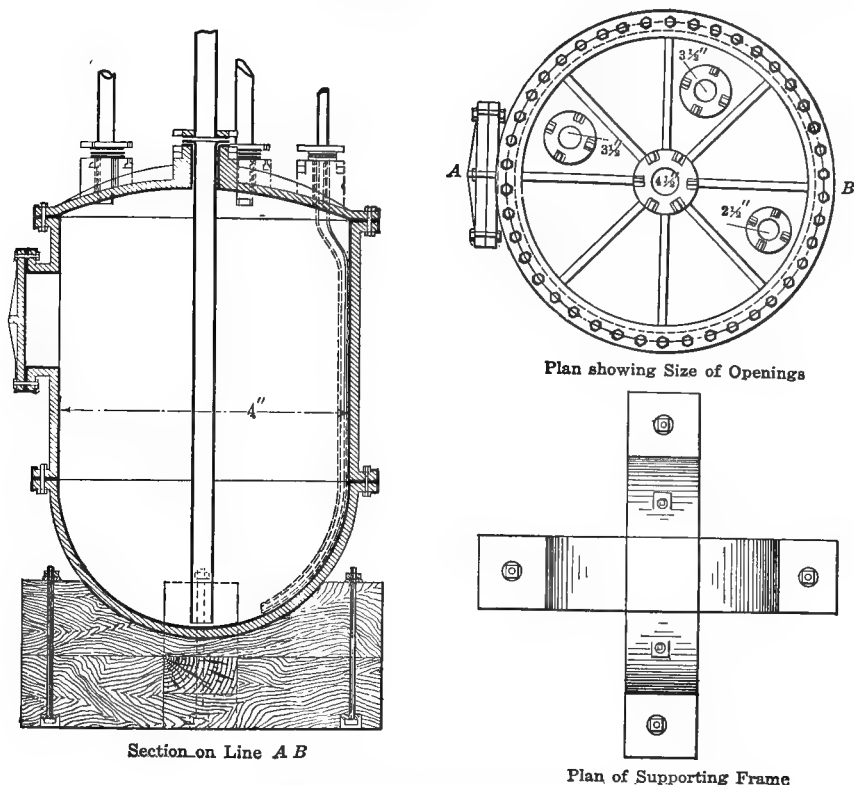
(4) REFINING OF COPPER-LIQUOR.—With the stirrer in motion the finished charge is drawn off into an upright pressure tank and forced with 40–50 lb. pressure through a filter-press. The cast-iron pressure tank is shown in Figs. 470–472; it is lined with lead, and the latter protected from wear by wood.<sup>3</sup> In filling the tank, some compressed air is admitted with the pulp in order to prevent the latter from packing. The filter press has hard-wood frames and plates 4 ft. sq., is 25 ft. long, and holds 5 tons of residue. The filtrate flows into a collection vat, from which it is elevated by means of a pressure-tank to the top of the refining tower, shown in Fig. 473, for the precipitation of  $Fe_2O_3$ , As, Sb, Bi, Ni, Co . . . . This purification is accomplished by adding CuO (really roasted copper matte) to the hot neutral solution of  $CuSO_4$ , through which is forced at the same time finely-divided air. The main reaction taking place may be expressed by  $FeSO_4 + \text{dissolved impurity} + O + CuO = Fe_2O_3 +$

<sup>1</sup> *Min. Ind.*, 1901, X, 232.

<sup>2</sup> At the works of Predazzo, it was found necessary to force compressed air through a perforated pipe placed at the periphery to prevent the roasted ore from packing. See also Megraw, *Eng. Min. J.*, 1912, xciv, 360.

<sup>3</sup> The tank used at Argentine had two 4-ft. cylindrical sections instead of the single one shown in the figure.

precipitated impurity +  $2\text{CuSO}_4$ ; some basic ferric and cupric salts are formed which remain in the residue. The latter is treated with dilute (2.5–3 per cent.)  $\text{H}_2\text{SO}_4$ , which dissolves only the Cu, and is filtered. The filtrate goes to the collection vat for the refining tower, the residue is worked with the residue of the solution tank. The refining tower, Fig. 473, is built of 4-in. staves of California redwood well bound by iron rods; it stands on a trestle and carries timbers anchored to the foundation by heavy guide-rods to guard against oscillation likely to be caused by the compressed air. The 4-in. air-inlet pipe is made of



FIGS. 470-472.—Cast-iron pressure-tank.

lead. Its horizontal arm enters the tower 18 in. above the bottom and is connected with a radial 6-in. lead pipe closed at the opposite end and perforated on the lower side. The vertical arm reaches to the top of the tower where it is joined through a valve to an iron pipe reaching down to the receiver of the air-compressor. This arrangement prevents the solution from running into the compressor when the latter is not in operation. Opposite the air-inlet is a 1-in. steam pipe held in the cast-iron door of the manhole; at right angles to it is the 4-in. discharge pipe provided with a hard-lead valve. On the top of the tower are a 4-in. inlet for solution and an 8-in. outlet for steam and air (not shown). The latter enters a lead-lined box with zigzag shelves to precipitate and carry

down particles of liquor entrained by the air. The upper third of the vat contains glass gauges to watch the filling.

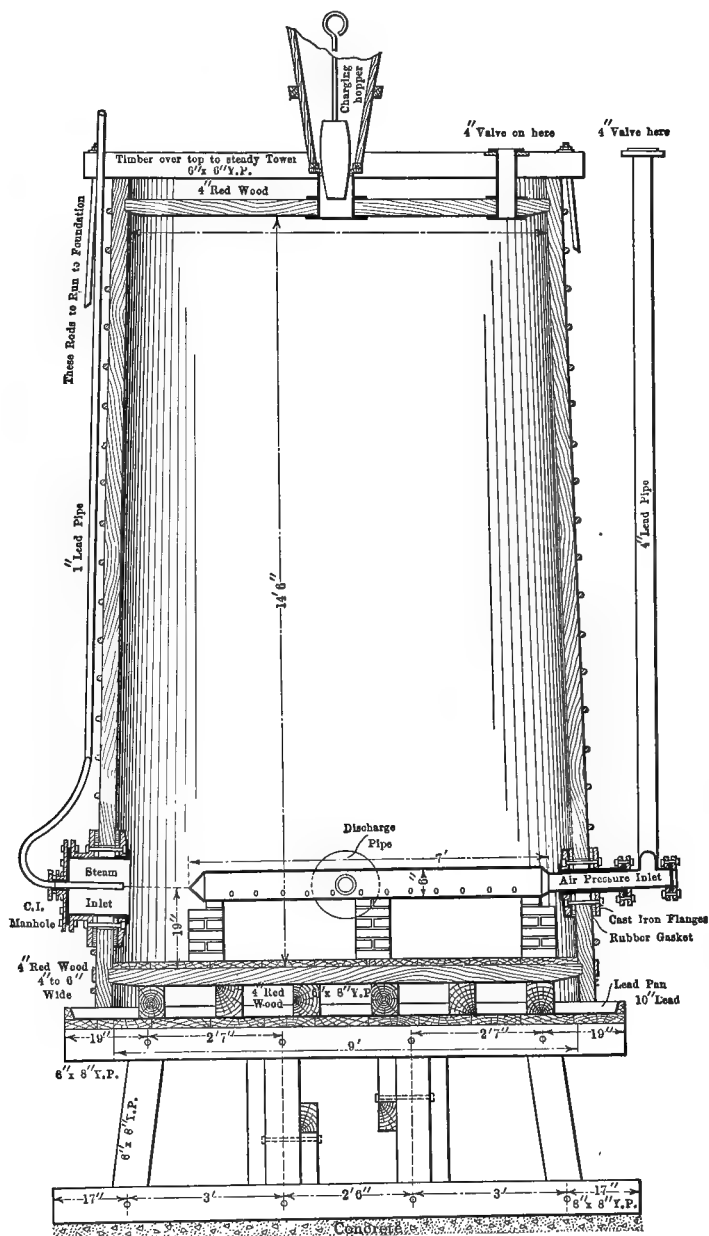
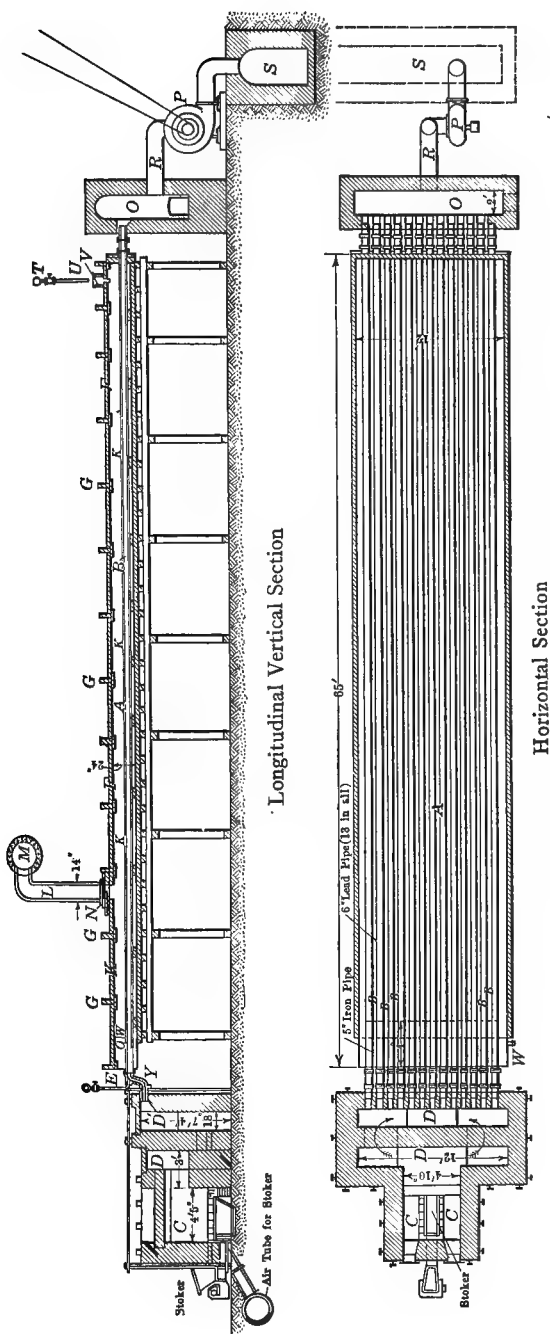


FIG. 473.—Refining tower.

In operating, the tower is charged with 5000 gal. liquor, steam is turned on as well as some air. The latter makes the heating proceed uniformly and causes



FIGS. 474-475.—Pan evaporator.

A, flat tank, 65 ft. long by 12 ft. wide by 2 ft. deep, of wood excepting 2 ft. near fire-place (of sheet iron), lead lined, more heavily at ends than at sides and bottom, rests on a trestle; B, thirteen 6-in. lead pipes immersed in liquor, enclosed at furnace end for 4 ft. by 5-in. iron pipe; C, fire-place with underfed stoker; D, dust-chamber; D', heat-distributing chamber; E, 13 cast-iron, S-shaped elbows connecting with the 13 lead pipes; each pipe has connection with compressed-air branch V to remove dust; O, brick suction chamber connected by galvanized iron pipe R with fan P discharging into underground flue S terminating in a 40-ft. brick stack; G, joists 5 ft. apart with cleats for support of roof, made up of boards; L, branch suction-pipe with slide-valve N connected with suction-main M, both of wood; fan with housing and wings of copper, shaft and arms of brass, delivers into wooden stack; V, feed-box with nipples; T, supply-pipe for copper liquor with branch-pipe U, W, 6-in. outlet-pipe for concentrated liquor, 4 in. above level of pipe B.

some basic ferric sulphate (not over 50 per cent. of the Fe present) to fall out. When the temperature of the liquor has reached  $70-80^{\circ}\text{C}.$ , more air is admitted, and some roasted matte fed. After from 3 to 4 hr., all the impurities will have been precipitated. The progress of the precipitation is followed by testing for Fe samples taken from a cock in the side wall. As soon as the solution is freed from Fe, all the other impurities will have been eliminated, as they fall out of solution before the Fe.

(5) EVAPORATION AND CRYSTALLIZATION.—The refined Cu-liquor, of  $24-26^{\circ}\text{Bé.}$ , and free from Ag (any dissolved  $\text{Ag}_2\text{SO}_4$  having been precipitated by  $\text{FeSO}_4$ ), goes to storage tanks. These supply the evaporators, in which the gases from a fire-place pass through tubes immersed in a flat wooden lead-lined tank, 65 ft. long by 12 ft. wide by 2 ft. deep, holding the Cu-liquor; the liquor travels in a direction opposite to that of the gases and the water vapor generated is drawn off by a suction-fan. The evaporator is shown in Figs. 474-475.

In operating, the pan is filled to the level of discharge pipe *W*, the fire started, and fan *P* set in motion; the level of the liquor is kept constant by occasional feeding from *T*. When the liquor near *W* is found to have reached the desired density of about  $30^{\circ}\text{Bé.}$ , weak liquor is turned on from *T*, and the amount to be fed regulated by hydrometer tests at *W*. The liquor from *W* flows into horizontal pressure tanks and is forced into covered troughs of California redwood,  $10\times 11$  in., for distribution to the crystallizing tanks. The troughs are in 16-ft. sections, which are butted together, the joints being made tight by rubber gaskets, iron flanges, and bolts. The boards of a section are joined with brass screws; the joints in it are made tight by a cement prepared by boiling together waste rubber, resin, linseed-oil, and ferric oxide.

The crystallization plant is shown in Fig. 476. There are two rows of tanks between which is a traveling rotatable belt elevator with copper cups, which raises the crystals, shoveled into the boot, and delivers them to the hopper. Here they drain and are discharged into the car below; the mother liquor collects in channels on the sides of the track and flows to a collecting pit.

The tanks are built of two 9-in. courses of acid-proof brick separated by a 2-in. space filled with a mixture of asphalt and sand. Each tank is 6 ft. deep and has a capacity of 720 cu. ft.; on top is a wooden frame carrying strips of lead 5 ft. long; crystals form on these as well as on the sides and the bottom of the vat. Crystallization requires seven days; when finished, the mother liquor is drawn off through brass tubes into the side-launders and flows to the collecting pit, whence it is elevated by pressure tanks to storage vats, to be used again in the solution tank and refining tower.

The frame with strips of lead and adhering crystals is raised by block and tackle; the crystals are knocked off and go with the side- and bottom-crystals to the elevator. The car receiving the crystals delivers them to a bin, whence they are fed to a crusher consisting of a fast-moving roll and a toothed stationary plate. The broken crystals are transferred to an inclined trough, washed with water, and sized in two hexagonal drums with brass shaft and arms and



maple sides having openings 0.375 and 0.125 in. in diameter. The undersize crystals with the wash-water go to dissolving tanks, the oversize are dried in a brass centrifugal machine. The crystals from the neutral solution retain their bluish color longer than do those from a slightly acid solution.

In order to reduce as much as possible the formation of small crystals, a tank filled with concentrated copper liquor is covered with a layer of water spread about 1 in. thick from a flat nozzle. This prevents the formation of small crystals on the surface (*salting out*) which sink to the bottom as soon as formed, a phenomenon caused by evaporation of the liquor on the surface.

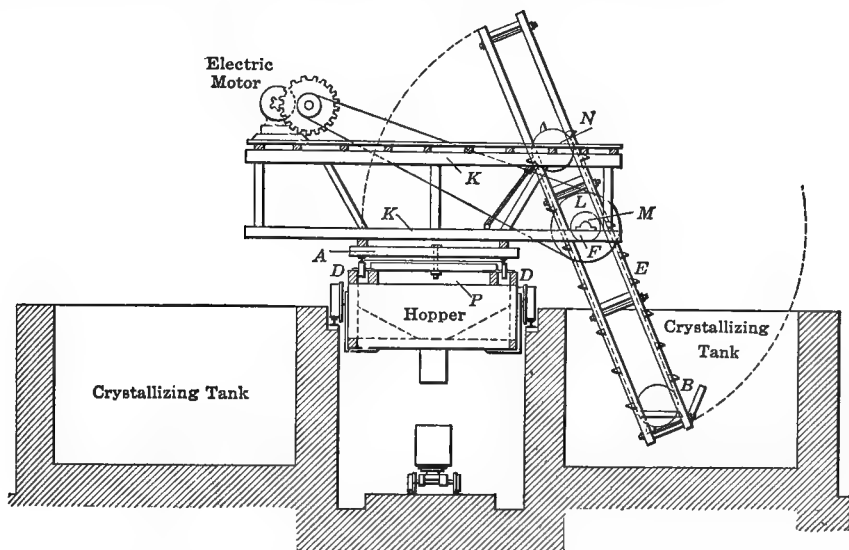


FIG. 476.—Crystallization Plant.

*K*, frame with turntable *A*, held by pin *P*, and circular track; *E*, belt elevator swinging on shaft *F*; *L* and *M*, pulleys for driving elevator pulley *N*; *B*, boot of elevator.

The plant at Argentine with a daily capacity of 60 tons of blue vitriol had: 3 Pearce furnaces, 8 solution tanks, 1 pressure tank, 5 filter-presses with storage tanks, 8 refining towers, 11 evaporators for 90,000 gal. refined copper liquor per day, and 112 crystallizing vats, each of 720 cu. ft. capacity.

### C. LEACHING METALLIC COPPER

**241. Leaching of Metallic Copper in General.**—The leaching of metallic Cu with  $\text{H}_2\text{SO}_4$  has many points in common with the similar treatment of copper matte. Leaching Cu has been replaced to a considerable degree by electrolysis, at least with pure metal.

Two processes have to be considered, the obsolete Augustin, and the Harz vitriolization which has retained its place as an independent process with impure Cu, and as an auxiliary process in the preparation of the blue-vitriol electrolyte in the electrolytic refining of Cu (§ 253, 264).

**242. The Augustin Process.**<sup>1</sup>—The underlying principles are the same as those for the treatment of copper matte, except that metallic copper is subjected to a chloridizing roast. The process was put into operation in 1885 by Klock and Hartmann in St. Louis, Mo., but details are lacking. The best example is probably that of Tajova<sup>2</sup> where the process was replaced in 1893 by electrolysis. Only the chloridizing roasting of metallic copper is of interest at present. Two grades of black copper were treated, containing: Cu 80–84, Ag 0.30–0.36, Sb 3–7 per cent., and Cu 70–80, Ag 0.20–0.25, Pb 9–15 per cent. The black copper tapped from the blast-furnace is ladled onto cast-iron plates, pulverized during solidification by rubbing with wooden hammers, and sifted through two screens. Of the three sizes obtained, the fine is ready for the furnace, the medium is ground in a buhrstone mill with 3-in. cast-iron grinding faces, and the coarse is first dry-stamped and then ground. The roasting-charge is made up to assay not over 7 per cent. Pb nor 0.4 per cent. Ag; it receives 15 per cent. salt. A charge of 500 lb. is dropped on to the upper hearth of a small two-hearth reverberatory furnace, and roasted at a dark-red with continuous rabbling for 7–10 hr.; it is then transferred to the lower hearth, where the rabbling is continued and 4 per cent. carbonaceous matter added in three portions at half-hour intervals to decompose  $x\text{MO} \cdot \text{As}(\text{Sb})_2\text{O}_5$ ; the temperature is then raised to a good red heat, and held there for 1.5–2 hr. Firing is now stopped and rabbling continued for 0.5–1 hr. more. The chloridized ore is raked up to a heap, remains untouched for 0.5 hr., and is then withdrawn, having gained 30–33 per cent. in weight. It is sifted while still warm (80° C.); any oversize is ground and added to the next charge. The chloridation of the Ag may be expressed by  $2\text{Ag} + 2\text{NaCl} + \text{CO}_2 + \text{O} = 2\text{AgCl} + \text{Na}_2\text{CO}_3$  and  $\text{Ag} + \text{CuCl}_2 = \text{AgCl} + \text{CuCl}$ . An addition of a small amount of  $\text{SiO}_2$  helps the chloridation.

**243. The Vitriolization Process.**<sup>3</sup>—The process in its present form was put into operation in 1858 at the Copper Smelter of Oker, Harz Mountains, and often goes by the name of Harz vitriolization. It is based upon the solubility of Cu in hot dilute  $\text{H}_2\text{SO}_4$  in the presence of air, and the relative insolubility of Ag, Au, Pb, As, Sb, etc. The leading steps are refining and granulating silver-bearing impure metallic Cu, dissolving the Cu granules in hot dilute  $\text{H}_2\text{SO}_4$  in the presence of air, separating the Cu-solution from the residue, crystallizing

<sup>1</sup> Augustin, *op. cit.*

Egleston, *Tr. A. I. M. E.*, 1876, IV, 295.

Capacci, *Rev. Un. Min.*, 1881, X, 201.

Howe, "Production Gold and Silver in the U. S.," 1883, p. 764.

<sup>2</sup> Markus, *Berg. Hüttenm. Z.*, 1852, XI, 5; 1855, XIV, 64.

Kerpely, *op. cit.*, 1871, XXX, 190, 285.

Wagner, *Oest. Zt. Berg. Hüttenw.*, 1873, XXI, 319.

Balling, C. A. M., "Metallhüttenkunde," Springer, Berlin, 1885, p. 358.

<sup>3</sup> Kuhlemann, *Zt. Berg. Hütten. Salin. Wesen i. P.*, 1871, XIX, 180.

Bräuning, *op. cit.*, 1877, XXV, 166.

Howe, "Production Gold and Silver in the U. S.," 1883, p. 790.

Egleston, *op. cit.*, 1884, p. 600.

Clement, *Min. Ind.*, 1900, IX, 278.

the  $\text{CuSO}_4 + \text{aq.}$  and converting it into marketable blue vitriol, and working up the insoluble residue.

(1) REFINING AND GRANULATING BLACK COPPER.—Black copper contains  $90 \pm$  per cent. Cu. The aim in refining is to scorify Pb, Fe, Ni, Co, Zn, etc., so as to prevent their being attacked or dissolved by the acid, as, when crystallizing with the blue vitriol, they would impair its quality. The slagging of Pb, Fe, and Zn is readily accomplished, that of Ni, Co and Bi (§ 193) less so. According to Egleston<sup>1</sup> the scorification of Ni(Co) is greatest at the period when Cu gives off the last of its S, hence some of the Ni in Cu can be concentrated in a small amount of slag. The curve of Wanjukow, Fig. 411, also shows that the elimination of Ni is rapid during the boiling period. A similar observation was made by Kuhlemann.<sup>2</sup>

The mode of operating is the same as in refining copper (§ 188 and foll.).

An analysis of granules from Altenau<sup>3</sup> gave Cu 95.00, Pb 2.71, Fe 0.07, Ni-Co-Zn 0.048, Sb 1.53, As trace, Ag 0.30 per cent. Granules ought to be flat, 1.2 in. in diameter, and have thin walls 0.02 in. thick; they resemble somewhat flaked breakfast-food; frequently they are rounded. The form of the granule depends upon the pitch of the Cu and the granulation proper. According to Egleston<sup>4</sup> the Cu ought to be granulated at the end of the boiling period, *i.e.*, when it has absorbed some  $\text{Cu}_2\text{O}$ , but has not yet reached the stage of set copper. At Oker<sup>5</sup> the metal is tapped before it has ceased boiling; at Freiberg<sup>6</sup> the same is the case; the reason being that the liberation of  $\text{SO}_2$  causes the walls to become thin.

The progress made in the refining of the black copper is carefully regulated toward the end in order to obtain just the pitch which is correct for granulating, as with the right pitch the granulation is simple and effective, while with a wrong pitch the granules are likely to be spherical and solid, and violent explosions are common. An excess of  $\text{Cu}_2\text{S}$  in the bath is indicated by films of  $\text{Cu}_2\text{S}$  flitting over the surface of the metal which has been freed from slag, and by the swelling of the slag when this is being skimmed. The excess is removed by charging small amounts of roasted white metal; or by rabbling or blowing. An excess of  $\text{Cu}_2\text{O}$  is indicated by the brightness of the surface of the Cu and the quickness with which the skimmed slag solidifies; a stick of sulphur thrown on the bath burns with the evolution of the brownish fumes of S-vapor. The excess of  $\text{Cu}_2\text{O}$  is removed by charging small amounts of white metal or of stick-sulphur. A granulated sample of Cu of the right pitch is pale red and shows no blackish specks, which indicate  $\text{Cu}_2\text{S}$ ; purplish granules indicate an excess of  $\text{Cu}_2\text{O}$ .

Beside the pitch, the temperature of the copper is of importance; the latter ought to be as low as will permit the metal to run in a thin stream from the tap-hole. The lower the temperature, the more effective is the expulsion of  $\text{SO}_2$ .

<sup>1</sup> *Tr. A. I. M. E.*, 1882, X, 49.

<sup>2</sup> *Loc. cit.*, p. 205.

<sup>3</sup> Kuhlemann, *loc. cit.*, p. 203.

<sup>4</sup> *Tr. A. I. M. E.*, 1875-76, IV, 296.

<sup>5</sup> Bräuning, *loc. cit.*, p. 163.

<sup>6</sup> Private Notes.

For granulating, the copper is run from the furnace in a thin stream into a deep covered water-tank, of wood, iron, or of brick, well cemented, let into the ground and provided with a steady inflow of cold water. On leaving the spout the copper either meets a strong jet of water which scatters the metal and thus assists in the forming of flat granules, or it drops on to a pole of green wood which breaks up the stream; in the latter case the basin is filled with hot water (Freiberg). The basin must be deep. Granulating with a jet of water requires cold water in order that the granules shall have become solid before they reach the bottom; if this is not the case, there is danger of serious explosions, and of the granules adhering to one another and forming lumps. The granulating basin is always covered, as explosions of more or less violence are always likely to occur. The basin must be deep enough so as not to be more than half filled with granules by a furnace charge. At Oker about 3 tons of copper are granulated in an oval wooden tank 8 ft. 2½ in. by 4 ft. 11 in. and 4 ft. 7 in. deep; at Freiberg about 10 tons in a circular boiler-iron tank 6 ft. 10 in. in diameter and 9 ft 10 in. deep. In the tank is placed a basket connected by chain or wire-rope with an overhead traveling-pulley to remove the granules and transfer them to the solution tank.

(2) DISSOLVING OF GRANULES.—The main reaction taking place in the solution of the copper is  $\text{Cu} + \text{H}_2\text{SO}_4 + \text{O} = \text{CuSO}_4 + \text{H}_2\text{O}$ ; a secondary reaction is  $2\text{CuSO}_4 + 2\text{Cu} = 2\text{Cu}_2\text{SO}_4$  and  $\text{Cu}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{O} = 2\text{CuSO}_4 + \text{H}_2\text{O}$ , *i.e.*, some of the  $\text{CuSO}_4$  formed by the main reaction acts upon Cu and is reduced to  $\text{Cu}_2\text{SO}_4$ , but the latter is oxidized again to  $\text{CuSO}_4$  in the presence of  $\text{H}_2\text{SO}_4$  and O. Thus the Cu is dissolved by the direct action of  $\text{H}_2\text{SO}_4$  and O, and the indirect action of  $\text{CuSO}_4$ .

The behavior of foreign metals with hot dilute  $\text{H}_2\text{SO}_4$  is similar to that in treating roasted matte. There will go into solution Cu, Zn, Fe, Ni, Co, and small amounts of  $\text{As}_2\text{O}_5$  and  $\text{Sb}_2\text{O}_5$ ; the residue will contain Ag, Au,  $\text{PbSO}_4$ , most of the  $\text{As}_2\text{O}_5$  and  $\text{Sb}_2\text{O}_5$ , some  $\text{Pb}_3\text{As}_2\text{O}_8$ , and basic sulphates of Sb, Sn, and Bi. The manner of operating varies considerably as shown in § 244 by several examples.

(3) CRYSTALLIZATION.—Trade demands that the crystals of blue vitriol shall be pure, large, and of a correct color. The conditions are fulfilled by having a clean and clear solution of the right concentration (28–29° Bé.) with not over 1 per cent. free acid, by a slow crystallization (six to eight days) in covered tanks in which are suspended strips of lead from cross-bars, by freeing the crystals from mother liquor through washing, and by drying the washed crystals. In allowing blue vitriol to crystallize out of solution in the usual way, large crystals form on the lead strips (similar to rock-candy on threads), smaller crystals on the sides of the tank, and the smallest on the floor. As the last bring only a low price, it is important to hinder their formation as much as possible; which is accomplished by the method of O. Hofmann given in § 240. Usually the bottom-crystals are redissolved and recrystallized.

(4) WORKING-UP OF INSOLUBLE RESIDUE.—This is briquetted and smelted in a suitable furnace for lead bullion or copper matte as the conditions may require.

**244. Examples of Vitriolization.** (1) OKER, HARZ MOUNTAINS. 1—Figs. 477-481 represent the leading apparatus in use at Oker. Fig. 477 gives the storage tank for acid, 11 ft. 10 in. by 6 ft. 5½ in. and 4 ft. deep, made of wood and lined with 8-10 lb. lead; it has a steam coil for heating, and siphons with roses for drawing off acid. The conical solution-vat, 5 ft. 3¼ in. high and 2 ft. 11 in. and 2 ft. 4¾ in. in diameter, also of wood and lined with 16-18 lb. lead, has at the side a discharge-spout, 8 in. square and 1 ft. 3 in. long. The false bottom is made of a heavy sheet of perforated lead carrying two blocks of wood, 6 in. high, boiled in oil, upon which rest bars of copper. The vat receives about 1 ton of granules, which fill it to a height of about 3 ft. 3 in. The solvent, H<sub>2</sub>SO<sub>4</sub> of 29-30° Bé. heated to 70° C., is sprayed on the copper for 5 min. and then shut off; now air is allowed to ascend through the warmed and acidulated copper for ½-¾ hr. to

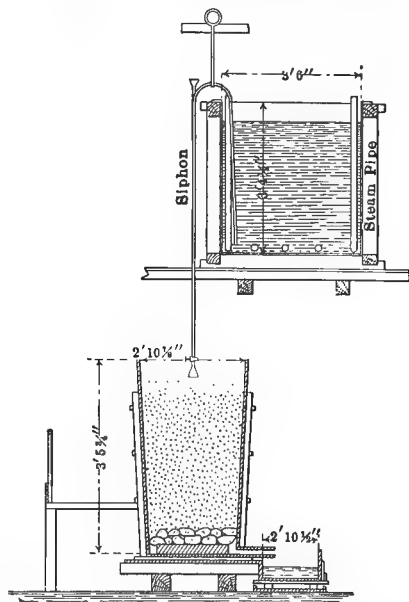


FIG. 477.—Acid-tank and solution-vat.

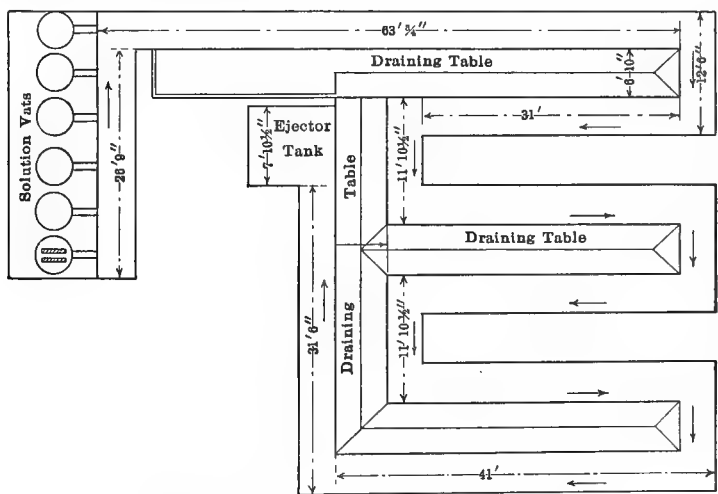


FIG. 478.—Solution-vats and crystallizing-troughs.

furnish the O necessary for the formation of CuSO<sub>4</sub>; acid is again admitted

<sup>1</sup> Bräuning, *Zt. Berg. Hütten. Salin. Wesen i. P.*, 1877, xxv, 165.

Egleston, "Production Gold and Silver in the U. S.," 1884, p. 600.

Private Communication, 1913.

for 5 min., in which time the  $\text{CuSO}_4$  will be washed down with the insoluble residue and will flow off through the discharge; the solution at first blue soon becomes colorless. The operations are repeated, and the dissolved granules replenished so as to keep the vat filled. A clean-up is made at intervals when the insoluble residue has choked up the open spaces between the copper bars, or when the bars have to be renewed. Six vats will handle about 600–800 lb. granules in 24 hr. An average analysis of the granules treated in 1902 gave: Cu 91.47, Ag 0.462, Au 0.0154, Pb 0.887, Bi 0.286, As 3.863, Sb 2.133, Fe 0.028, Ni-Co 0.750.

From a unit of six dissolving vats, Fig. 478, the copper solution and insoluble residue pass through a series of zigzag launders, 347 ft. 4 $\frac{5}{8}$  in. long, in which the insoluble part sinks to the bottom and blue vitriol crystallizes owing to the cooling effect of the air. Most of the mud sinks to the bottom in the head launder; the vitriol collecting near the tail-end is rich in  $\text{CaSO}_4$ ,  $\text{Pb}_3\text{As}_2\text{O}_8$ ,  $\text{Pb}_3\text{Sb}_2\text{O}_8$ . The mother liquor flows from the last launder into a collection tank, 7 ft. 10 $\frac{1}{2}$  in. square, whence it is raised by an injector to the storage tank for solvent, to be brought to the right concentration by addition of chamber acid (50° Bé.). In 1904 a liter mother liquor (specific gravity 1.719) contained in g: Cu 15.000, Ni 22.980, Fe 3.052,

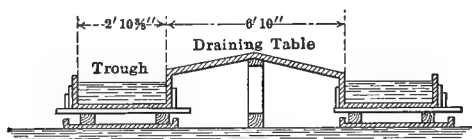
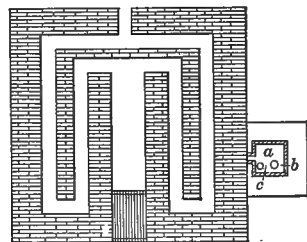
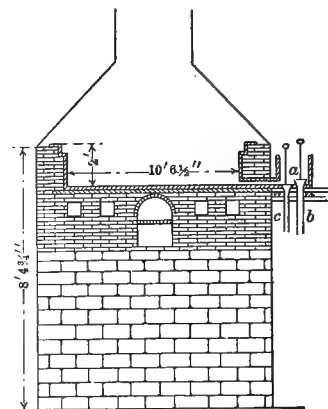


FIG. 479.—Vitriolization at Oker, Germany.



FIGS. 480–481.—Concentration-pan.

free  $\text{H}_2\text{SO}_4$  203.880. A cross-section through a launder is given in Fig. 479: two wooden lead-lined launders are separated by a gable-shaped division covered with sheet lead. The crude vitriol is shoveled out once a week onto the sloping planes of the division from which the mother liquor flows back into the launder. The vitriol is washed superficially at intervals with clean water to remove adhering acid mother liquor.

The crude vitriol, which is unsightly and encloses insoluble residue as well as mother liquor, has to be purified. It is removed to a lead pan shown in Figs. 480–481, dissolved in weak mother liquor, and the mud allowed to settle. The pan, 11 ft. 6 in. long by 10 ft. 10 $\frac{1}{2}$  in. wide and 1 ft. 11 in. deep, is of  $\frac{3}{8}$ -in. lead; it rests on  $\frac{3}{4}$ -in. cast-iron plates, beneath which are heating-flues for the passage of the gases from the fire-place. The pan is charged to a depth of 1 ft. 3 $\frac{3}{4}$  in. with mother liquor and water, to density of 18–19° Bé., and heated to 70° C.; crude

vitriol is stirred in and dissolved in about 1 hr. until the liquor has been raised to 28° Bé. Some fine sheet copper used to be added to the pan-charge to precipitate traces of Ag that might have gone into solution. At present an emulsion of ground galena is added for this purpose. The fire is withdrawn from the grate, the pan is covered with boards to retard the cooling, and the mud allowed to settle 6 to 8 hr. The clear copper liquor, still at 50° C., is withdrawn through the upper tap, *b*, into wooden lead-lined crystallizing tanks, 9 ft. 6 in. long by 4 ft. 7 in. wide and 3 ft. 3 in. deep, in which are suspended strips of lead, 0.15 in. thick and 0.78 in. wide, from 25 cross-bars, five to a bar, reaching to near the bottom. The crystallization, which must be slow if well-developed crystals are to form, lasts from 8 to 12 days.<sup>1</sup> The largest crystals form on the strips, then follow the side-, and lastly the bottom-crystals. Strip- and side-crystals are washed with water to remove adhering mother liquor, drained on inclined tables (better in a centrifugal machine), dried for eight days in a dark room on shelves 6 ft. 6 in. wide at a temperature ranging from 20 to 25° C. (above 25° C. the transparent crystal becomes opaque), sorted according to size, and barreled. Bottom crystals are recrystallized. An analysis of blue vitriol of Altenau, where the mode of operating is the same as at Oker, gave  $\text{CuSO}_4 + \text{aq}$ , 99.9700, Fe 0.0107, Sb 0.0123, As 0.0064, Ag 0.0006, Zn trace, Ni trace.<sup>2</sup> The blue vitriol produced in 1900 is less pure; it analyzed: Cu 24.721, Fe 0.054, Ni 0.255, Co trace, As 0.068, Sb trace, Bi none, Ag 0.0015, free  $\text{H}_2\text{SO}_4$  0.913 per cent. The yield of Cu in the form of blue vitriol is 99.76 per cent.; that of Ag is 99.4 per cent. The mother liquor from the crystallizing tanks serves to dissolve crude vitriol. The residue in the concentration pan is withdrawn at intervals through the lower tap, *c*, which is flush with the bottom, washed with water, filter-pressed, dried, and smelted with a lead charge. The residue produced in 1901, forming 17.5 per cent. of the weight of the granules, averaged Ag 4.010, Au 0.1066, Cu 1.38 (1.15 as  $\text{CuSO}_4$ ), Pb 16.08, Bi 8.02, As 17.06, Sb 19.71, Fe 0.23, NiCo 0.45,  $\text{SO}_3$  10.28,  $\text{H}_2\text{O}$  0.95, Insol. 2.62 per cent. The mother liquors are used over and over until they become so heavily charged with Fe and Ni that they interfere with the purity of the blue vitriol; they are then worked for Cu and Ni.

A unit of 6 solution vats, 2 concentration pans, and 24 crystallizing tanks produces per day 3000 lb. blue vitriol; 100 lb. Cu give 380 lb.  $\text{CuSO}_4 + \text{aq}$ , require 160 lb.  $\text{H}_2\text{SO}_4$  of 50° Bé., and about 310 lb. coal.\*

(2) FREIBERG, SAXONY.<sup>3</sup>—The solution vessel is a lead-lined wooden tank, 4 ft. 11½ in. square and 5 ft. 11 in. high. On the true bottom is placed an inclined floor of gypsum, and this covered with sheet lead with edge turned up and beaten against the sides. The bottom is 5½ in. thick on one side and tapers to the discharge opposite, to facilitate the removal of insoluble residue. The vessel has a false bottom of perforated (0.4-in. conical holes) sheet lead, 7¼ in. above the true bottom, supported by posts. The discharge is in the side on

<sup>1</sup> See Hofmann's addition of water, § 240.

<sup>2</sup> Kuhlemann, *loc. cit.*, p. 213.

<sup>3</sup> Private Notes.

the true bottom. A steam injector under the false bottom furnishes the air and heat necessary for the solution of the copper; the  $\text{H}_2\text{SO}_4$  of  $12^\circ$  Bé. and  $60\text{--}75^\circ$  C. is sprayed on the granules by a rotary feeder working upon the reaction-wheel principle. This Haege wheel has a small glass disc on the lower side and rotates on a needle attached to a lead-covered iron bar placed across the vat. The vat holds 5 tons granules assaying Cu 97.98 and Ag 0.3–0.4 per cent. An analysis of 1905 gave: Au 0.0051, Ag 0.38, Cu 97.78, Pb 0.27, Bi 0.14, Fe 0.12, Ni 0.09, Co 0.03, As 0.33, Sb 0.47, Sn trace, Insol. 0.12, S 0.10, O 0.13 per cent. According to the desired rate of working, governed in part by the concentration of the acid, there are treated in a vat from 1650 to 3300 lb. granules in 24 hr.; the acid correspondingly contains from 110 to 400 g.  $\text{H}_2\text{SO}_4$  per liter ( $=12\text{--}28^\circ$  Bé.).

The copper liquor produced from 37–200 g.  $\text{H}_2\text{SO}_4$  has a density of  $32\text{--}35^\circ$  Bé. and averages 35–40 g. free  $\text{H}_2\text{SO}_4$  in a liter. The copper liquor flows into settling tanks having partition walls to retard the current and to force it to pass through and not simply along the top of the tank. The clarified liquor is crystallized; the crystals are freed from mother liquor, washed and dried in a centrifugal machine; they contain 0.025 Fe, 0.012 Ni, from 0 to 0.10 per cent. free  $\text{H}_2\text{SO}_4$ , and are free from As and Sb. The mother liquor contains in a liter 1.026 g. Fe, 2.416 NiCo, 0.035 Bi, 5.87 As, 0.529 Sb, 0.049 g. Pb. The insoluble residue is drained, washed with hot water, filter-pressed, treated with water in the press until the effluent measures  $2\text{--}3^\circ$  Bé., and dried. It assays Ag 5–6.5, Pb 7, and Cu 40–65 per cent. It is roasted sulphatizingly in a muffle furnace until a leaching test shows that the water-soluble  $\text{CuSO}_4$  has been removed from the residue down to 0.2–0.3 per cent. Cu. The roasted residue is treated with hot dilute  $\text{H}_2\text{SO}_4$  in the presence of sheet copper to decompose all  $\text{Ag}_2\text{SO}_4$  that may have been dissolved. The resulting second residue, after washing and drying, assays Au 0.28, Ag 22.5, Pb 28, Cu 0.2–1.0 and Bi 0.1–10.0 per cent.; and is charged on the lead bath of a cupelling furnace.

Of the Cu charged there is recovered in the blue vitriol 99.85, in the residue 0.05, in the dross 0.10 per cent. There are produced per day about 30,000 lb. blue vitriol. The plant consists of the following parts: (1) *Solution of Granules*: 3 acid tanks, 4 solution vessels, 2 small and 4 large clarifying tanks, 6 collecting tanks for liquor of  $32^\circ$  Bé. (2) *Retreatment of Vitriol*: 2 solution tanks, 3 clarifying tanks, 1 residue tank. (3) *Treatment of Residue*: 2 acid tanks, 1 solution vessel, 2 drying boxes, 1 filter-press, 1 muffle furnace for roasting, 1 collecting tank for residue, 1 collecting tank for liquor, 1 filtering box. (4) *Crystallization*: 150 tanks. (5) *Drying of Blue Vitriol*: 2 centrifugal machines, 1 tank for liquor. (6) *Additional*: 1 compressor, acid-eggs, collecting tanks for mother liquors and acid.

(3) EASTERN UNITED STATES.<sup>1</sup>—The solution tank ("oxidizer," "dissolver") for granulated copper is usually 3 ft. by 3 ft. 3 in. in diameter and 6 ft. 6 in. high; it is of wood lined with 15-lb. lead, and has an opening 1 ft. square in the front

<sup>1</sup> Clemmer, *Min. Ind.*, 1900, ix, 277.



near the bottom; a false bottom of  $\frac{3}{4}$ -in. iron pipes, covered with heavy lead pipe and closed at the ends by overlapping lead, rests 1 ft. above the true bottom upon acid-proof brick. The granulated copper filling the tank is covered by an acid-distributor which is a piece of sheet-lead having up-turned edges and two  $\frac{1}{4}$ -in. holes per square inch surface. The acid, of  $10^{\circ}$  Bé. and  $80^{\circ}$  C., is fed by the oscillating trough, 34 in. long and 15 in. wide, shown in Fig. 482. It is made of 1-in. boards, the axis *F* extends 3 in. beyond the trough; *G* and *D* are stops. The copper solution flows from the dissolving tank into a receiving vessel and is circulated until it measures  $34\text{--}35^{\circ}$  Bé. at  $16^{\circ}$  C.; it is then run into a settling tank and thence into a crystallizing vat. The copper in the solution tank is replenished without shutting off the acid; once a month the solution tank is washed out by water under pressure. The slime collecting under the false bottom and in the settling tank is removed periodically. Six solution tanks

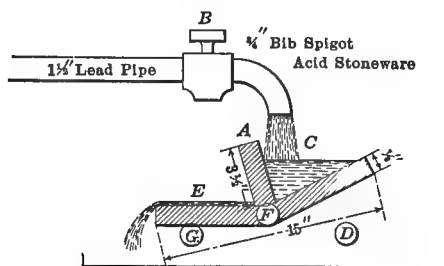


FIG. 482.—Oscillating feed-trough.

furnish 5000 lb. blue vitriol per day, for which 10 crystallizing vats 10 ft. square and 3 ft. deep are necessary. The crystallizing tanks are of wood, lined with 8-lb. lead on the sides and 10-lb. lead on the bottom; the sides often receive a taper of 1 in. to prevent buckling of the lead. The mother liquor is drawn from the bottom through an opening having a plug-seat and plug of hard lead (10 per cent. Sb).

At the end of the crystallization (which favors layering), it is sometimes advantageous to draw off the top (or lighter) liquor separately from the bottom (or heavier) liquor which is richer in  $\text{CuSO}_4$ , and recover the Cu from the lighter by means of Fe. The crystals from a tank are dried by passing them through a housed revolving brass screen with  $\frac{1}{4}$ -in. holes; the chamber is heated by live steam and is connected with a suction fan to draw off the vapors. The crystals are fed continuously into the screen, the fines are sifted out to be redissolved, and the coarse crystals ( $> \frac{1}{4}$  in.) are discharged direct into packing barrels.

A plant is usually terraced. On the top-level are the acid tanks, lined with 10-lb. lead and provided with steam-coils; next come the dissolving tanks; these are followed by receiving and settling tanks lined with 8-lb. lead; on the fourth level or ground floor are the crystallizing vats in double rows with a 2-ft. passage way, and the wash-floor for crystals, covered with 10-lb. lead. The mother-liquor tanks, lined with 8-lb. lead, and the sump, lined with 6-lb. lead,

are let into the ground floor; drainage gutters leading to the sump are lined with 6-lb. lead.

The cost of producing 5000 lb. blue vitriol per day near New York City in a plant which manufactures acid and smelts copper was 3.73 cents per pound in 1900; the totals were: Copper and acid \$152.63; foreman and labor \$11.50; packing \$4.80; fuel \$9.00; repairs, insurance, depreciation, etc., \$6.00; in all \$183.93.

(4) SPECIAL FORMS OF OXIDIZERS IN THE EASTERN UNITED STATES.—

(a) Works A.—The solution vessel is made up of two flanged sections of glazed sewer-pipe, 2 ft. 10 in. high and 3 ft. 4 in. inner diameter. The lower section rests on a heavy flanged lead plate with  $1\frac{3}{8}$ -in. holes, covered with 6 in. of slag serving as a support for the granules. On the upper section is placed a wooden frame supporting a flanged lead plate with  $\frac{3}{8}$ -in. holes. Hot acid is admitted periodically onto the distributing plate through a circular lead pipe, having perforations on the inner side, by mechanically opening and closing a cock.

(b) Witherell Down-draft Oxidizer.—A wooden lead-lined tank, 12 ft. in diameter and 6 ft. 6 in. deep, has a radial grate surface, 3 ft. 6 in. down from the top, and in the center a suspended ventilating chimney, 30 in. in diameter. The grate is filled with granules to 6 in. from the top of the tank; hot acid is turned on periodically through two radial horizontal wooden troughs, with staggered holes, moving around the chimney. Steam is admitted at intervals. The copper liquor overflows through a trapped discharge-spout. When the granules have been dissolved down to 12–18 in. from the grate, the suspended chimney is raised, a man enters the tank, shovels over the granules, and removes the mud with a hose. The tank is then recharged.

(c) The Walker Dissolving Machine.—In order to hasten the solution of granules, A. L. Walker<sup>1</sup> introduced at the Perth Amboy plant of the American Smelting & Refining Co. his mechanical device, by means of which copper granules are alternately immersed in and withdrawn from a tank holding hot dilute  $H_2SO_4$ , fresh acid being fed and copper-liquor removed continuously. The essential parts are: (1) three walking beams, set at  $180^\circ$ , having at one end an arc-shaped piece, at the other a pitman driven from an eccentric; (2) a stout basket of hard-lead, 6×4 ft. and 1 ft deep, charged with 1 ton of copper granules, carried by a lead-covered copper frame which is suspended by a chain riding on the arc-shaped piece, and immersed vertically in (3) a solution-tank, 15 by 15 ft. and 5 ft. deep, provided with a steam-coil and a vertical partition reaching to near the floor, which separates the immersion-division, fed continuously with dilute  $H_2SO_4$  so as to have 10 per cent. free acid, from the discharge-division provided with an outlet for the continuous outflow of concentrated copper-liquor. The movement of the walking-beam is so apportioned that the basket remains half a minute in the air for the purpose of oxidation and is immersed for a half minute in the tank for the purpose of solution. The outflowing copper-rich liquor runs through a series of lead-lined

<sup>1</sup> U. S. Patent No. 788862, May 2, 1905.

launders, 24 in. wide and 6 in. deep with wooden sides and sheet-iron bottom in which small crystals of blue vitriol separate, and enters a second solution tank equipped in the same manner as the first and 10 in. below it. The copper-liquor from the second tank passes through a second series of launders where crystallization again takes place, and enters a third solution-tank whence the copper-liquor passes into a third series of crystallizing launders. As the three solution-tanks are provided with steam-coils and evaporation takes place all the time, the liquor leaving the third series of crystallizing launders is very much reduced in volume. It is fortified with acid to bring the free  $H_2SO_4$  to the standard 15 per cent. and returned to the first solution-tank. The small crystals and the insoluble residue settling in the crystallizing launders are removed at intervals, charged into ordinary tanks where the crystals are dissolved in hot water and the mud is settled. The clear blue-vitriol solution is run into crystallizing tanks, and the mud carrying precious metal is worked up in a suitable manner. The granulated copper is dissolved six times as fast as by the ordinary method using a steam-injector. The method was abandoned in 1907, but put into service again later on.

## CHAPTER IX

### ELECTROLYSIS OF COPPER

**245. In General.**—The raw materials from which Cu might be extracted by means of an electrolytic process are ore, matte, speise, and lastly metal which is to be refined to a higher degree than is practicable by dry methods.

**246. Electrolysis of Ore.**—All direct as well as most indirect processes have been failures. A direct process is one in which the ore forms the anode. The reasons why such a treatment cannot be successful have been given in § 156. An indirect process is one in which the raw or roasted ore is treated with a solvent, and the solution electrolyzed, not in contact with ore. The methods advocated by Laszcynski (§ 205), Carmichael (§ 206), Greenawalt (§ 207), Siemens-Halske (§ 218), Hoepfner (§ 222) have already been discussed.

**247. Electrolysis of Copper Matte.**<sup>1</sup>—After the electrolytic refining of metallic copper had proved a commercial success, it seemed natural to go one step back and attempt the electrolysis of copper matte in a bath of acidulated blue vitriol with cast matte as anode and sheet copper as cathode. This process was patented by Marchese in 1882<sup>2</sup> and carried out on a large scale with 30-per-cent. matte at the Casarza works near Sestri-Levante, Genoa,<sup>3</sup> and proved a failure. Later it was taken up again at Stolberg, Westphalia,<sup>4</sup> with matte of 15–16 per cent. Cu, but proved again to be unsuccessful. It was held that the matte would be decomposed in part by electrolysis, in part by the  $\text{Fe}_2(\text{SO}_4)_3$ , formed in the bath, and that a potential of about 1 volt would be sufficient for the work. The process failed because the e.m.f. required reached 5 volt.; because the anode became coated with non-conducting matter (S); because decomposition was unequal and disintegration of the anodes followed; because more Cu plated out than went into solution and the electrolyte was enriched in  $\text{FeSO}_4$ , which offered a greater resistance than  $\text{CuSO}_4$  and required frequent renewal of the bath; because the character of the deposited Cu was inferior; and because the deposited Cu was redissolved by the  $\text{Fe}_2(\text{SO}_4)_3$  formed.

The remarks in § 205–207, 218 and 222 relating to the processes for treating ore hold good also for matte.

In order to make electrolysis of matte in aqueous solution successful, it is necessary that the matte be nearly pure  $\text{Cu}_2\text{S}$  which leaves behind only a small

<sup>1</sup> Borchers-McMillan, *op. cit.*, p. 247.

<sup>2</sup> *Rev. Un. Min.*, 1883, XIV, 331; 1884, XV, 668, 1885, XVII, 563.

<sup>3</sup> Badia, *La lumière électrique*, transl. in *Sc. American Supplement*, 1885, XIX, 7623, 7646, Nos. 478 and 479; also *Berg. Hüttenm. Z.*, 1885, XLIV, 330; *Eng. Min. J.*, 1885, XL, 21.

Zopetti, *Il Politecnico*, Nov. and Dec., 1885, transl. in *Rev. Un. Min.*, 1886, XIX, 197; XX, 94; also *Berg. Hüttenm. Z.*, 1886, XLV, 207, 221, 538.

<sup>4</sup> Cohen, *Berg. Hüttenm. Z.*, 1888, XLVII, 406; 1894, LIII, 328; *Zt. Electrochemie*, 1894, p. 50.

amount of residue (S), and at the same time will not contaminate the electrolyte with impurities (Fe). This has been done at Mansfeld, Germany, with the Borchers-Franke-Günther process.<sup>1</sup> The matte with Cu 72-76 per cent. is cast into anodes, 40 in. square by 2 in. thick, which have to be annealed to prevent their cracking. They are suspended in parallel alternating with Cu cathode sheets in the usual wooden lead-lined electrolyzing vat for metallic copper, by T-shaped pieces of Cu imbedded in the matte and tinned at the ends. The electrolyte is an acidulated solution of blue vitriol held at 70° C., circulated and aerated; the current density 7 amp. per square foot at a pressure of 0.75 volt. The Cu is dissolved and goes to the cathode, S and other insoluble matter go into the anode mud; if the current density is too low, only half of the Cu goes into solution. The anode has to be removed before it becomes too thin and begins to crumble. The mud is filter-pressed, treated with a hot solution of acetylene tetrachloride to dissolve the S, which separates upon cooling, and then worked by the Ziervogel process (§ 237) to recover the Ag. While metallurgically the process was successful, the cost of treatment was too high; the process was therefore abandoned.

**248. Electrolysis of Speise.**—Considering that all attempts at the electrolysis of ordinary copper matte have been unsuccessful, it is not to be expected that a similar treatment of speise will be anything else but a failure. A process was suggested by André in 1877,<sup>2</sup> but there is no record of anything more.

**249. Electrolysis of Metallic Copper in General.**<sup>3</sup>—The aim of the electrolytic refining of copper is to produce pure copper from a high-grade blister copper by means of the selective chemical action of the electric current. The current is intended to dissolve copper from the blister copper suspended as anode in a solution of  $\text{CuSO}_4$  acidulated with  $\text{H}_2\text{SO}_4$ , and to deposit it on a copper cathode. Most of the usual impurities will remain behind and form the anode mud, some will be dissolved and become concentrated in the electrolyte, some may be deposited on the cathode.

The possibility of such a process was proved experimentally in 1847 by von Leuchtenberg, but its industrial applicability was first recognized by

<sup>1</sup> Wagner-Primrose, *Eng. Min. J.*, 1907, LXXXIV, 673.

Editor, *Metallurgie*, 1908, v, 29.

<sup>2</sup> *Dingl. Polytech. J.*, 1879, CXXX, 281; 1880, CXXXVI, 415.

<sup>3</sup> T. Ulke, "Modern Electrolytic Copper Refining," Wiley, New York, 1903. W. Borchers and W. G. McMillan, "Electric Smelting and Refining," Lippincott, Philadelphia, 1904, p. 187-245. J. Billiter, "Die Electrochemischen Verfahren der Chemischen Grossindustrie." Knapp, Halle, 1909, I, pp. 37-139. Keller, *Min. Ind.*, 1898, VII, 229. Crocker-Arendt, *School Mines Quart.*, 1903, XXV, 3. Bancroft, *Tr. Am. Electrochem. Soc.*, 1903, IV, 175; *Electrochem. Ind.*, 1902-03, I, 484, 584; *Mines and Minerals*, 1903, XXIV, 182, 229; *Eng. Min. J.*, 1903, LXXVI, 740; *Metallurgie*, 1904, I, 670. Schwab-Baum, *Jl. Phys. Chem.*, 1903, VII, 493. Burgess, *Tr. Am. Electrochem. Soc.*, 1905, VII, 51; *Electrochem. Metal. Ind.*, 1905, III, 173. Addicks, *Jl. Franklin Inst.*, 1905, CLX, 421; *Min. Sc. Press*, 1906, XCII, 38. Bennett, Electrodeposition (plating) of Copper, *Tr. Am. Electrochem. Soc.*, 1913, XXXI, 233; *Met. Chem. Eng.*, 1913, XI, 284. Burns, *Tr. A. I. M. E.*, 1913, XLVI; (Great Falls Plant); Discussion, *Met. Chem. Eng.*, 1913, XI, 670 (Motherwell, Burns).

Elkington who patented in 1865 the multiple system of the process, and erected the first successful plant in 1869 at Pembrey, Wales. His example was soon followed by others in England, Germany, and elsewhere. In the United States the Balbach Smelting & Refining Co.<sup>1</sup> in 1883 was the pioneer of the industry, which has grown to such a degree that in 1912, with the United States furnishing over one-half of the world's copper, 81 per cent. of its product was electrolytic copper.

The second form of the process in operation to-day is the Hayden or Series System introduced in 1886.

Table 115<sup>2</sup> gives the leading works of the United States and their capacities.

TABLE 115.—ELECTROLYTIC COPPER REFINERIES OF THE UNITED STATES

Works	Location	Process	Capacity million pounds
Nichols Copper Co. ....	Laurel Hill, N. Y. ....	Series. ....	330 <sup>3</sup>
Raritan Copper Works. ....	Perth Amboy, N. J. . .	Multiple. ....	360 <sup>4</sup>
Baltimore Copper Smelting & Rolling Co. ....	Canton, Md. ....	Series and multiple.	312 <sup>5</sup>
American Smelting & Refining Co. ....	Maurer, N. J. ....	Multiple. ....	192 <sup>b</sup>
U. S. Metals Refining Co. ....	Chrome, N. J. ....	Multiple. ....	180 <sup>5</sup>
Balbach Smelting & Refining Co. ....	Newark, N. J. ....	Multiple. ....	48 <sup>5</sup>
Anaconda Copper Mining Co. ....	Great Falls, Mont. ....	Multiple. ....	65 <sup>5</sup>
Tacoma Smelting Co. ....	Tacoma, Wash. ....	Multiple. ....	36 <sup>5</sup>
Calumet <sup>4</sup> & Hecla Mining Co. ....	Buffalo, N. Y. ....	Multiple. ....	55 <sup>5</sup>

When  $\text{CuSO}_4$  is dissolved in acidulated water, it is in part dissociated into  $\text{Cu}^{++}$  and  $\text{SO}_4^{--}$  ions. If the solution is electrolyzed using copper electrodes, the  $\text{SO}_4^{--}$  ions migrate to the anode, are deposited, give up their charges to the anode, and combine with an equivalent amount of copper. Similarly, the  $\text{Cu}^{++}$  ions migrate to the cathode, give up their charges to the cathode, and are deposited as metallic copper.

Another way of expressing the same idea is that the Cu at the anode receives two positive charges ( $\text{Cu} + 2+ = \text{Cu}^{++}$ ), is converted into  $\text{Cu}^{++}$ , and goes into the solution; at the cathode the two positive charges of  $\text{Cu}^{++}$  are neutralized by two negative charges of the current ( $\text{Cu}^{++} + 2- = \text{Cu}$ ), and Cu falls out of solution. The second statement shows that in a process with soluble copper electrodes there is only a transference of Cu from anode to cathode, hence there is required little energy or only a small electromotive force to set in motion, by overcoming the resistance of the solution, large quantities of Cu or  $\text{SO}_4$  on their paths to the cathode, or anode. The quantity of current,

<sup>1</sup> Ulke, *Electrochem. Ind.*, 1903, 1, 240.

Editor, 1904, II, 303.

<sup>2</sup> *Min. Ind.*, 1912, XXI, 288.

<sup>3</sup> Estimated.

<sup>4</sup> To be increased to 480,000,000 lb.

<sup>5</sup> Official figures,

on the other hand, has to be proportional to the number of  $\text{Cu}^{++}$  ions, or, in industrial work, the amperage will be high as compared with the voltage. This regularity of equal solution at anode and deposition at cathode may be disturbed by the formation of  $\text{Cu}_2\text{O}$ <sup>1</sup> with a low current density, e.g., if below 0.09 amp. per square foot. Here  $\text{Cu}^{++}$  ions in the electrolyte, instead of receiving two negative charges ( $\text{Cu}^{++} + 2- = \text{Cu}$ ), receive only a single one ( $\text{Cu}^{++} + 1- = \text{Cu}^{\cdot}$ ), with the result that  $\text{CuSO}_4$  is reduced only to  $\text{Cu}_2\text{SO}_4$  instead of to Cu, and  $\text{Cu}_2\text{SO}_4 \rightleftharpoons \text{Cu} + \text{CuSO}_4$  or  $2\text{Cu}^{\cdot} \rightleftharpoons \text{Cu} + \text{Cu}^{++}$ . This disturbance is favored by a high temperature and a high concentration of the electrolyte. It forms the explanation<sup>2</sup> of the fact that in the electrolysis of copper in  $\text{CuSO}_4$ -solution there is always set free finely divided Cu which collects in the anode mud and causes this to assay 40–50 per cent. Cu. But  $\text{Cu}_2\text{SO}_4$  may be and is in part converted into  $\text{CuSO}_4$  by the reaction  $\text{Cu}_2\text{SO}_4 + \text{O} + \text{H}_2\text{SO}_4 = 2\text{CuSO}_4 + \text{H}_2\text{O}$ , and this is one of the reasons for the neutralization of the free acid in the electrolyte.

**. 250. Behavior of Individual Impurities.**—In industrial electrolysis the anode is not pure copper, but blister copper with 98+ per cent. Cu. The behavior of impurities likely to occur in such material was first studied by Kiliani<sup>3</sup> with a solution containing 15 per cent.  $\text{CuSO}_4 + 5$  aq (= 3.81 per cent. Cu) and 5 per cent. free  $\text{H}_2\text{SO}_4$ , with a current density of 1.8 amp. per square foot, and an electrode distance of 2 in. Though the composition of this electrolyte resembles that in use at present, the current density is very low; nevertheless the data of Kiliani may serve as a general guide, and will be supplemented by later information.

According to their behavior in general, impurities are conveniently grouped under four heads:

- I. Ni, Co, Fe, Mn, Zn, Pb, Sn.
- II. Au, Ag, Pt, Se, Te.
- III.  $\text{Cu}_2\text{O}$ ,  $\text{Cu}_2\text{Se}$ ,  $\text{Cu}_2\text{Te}$ ,  $\text{Cu}_2\text{S}$ .
- IV. As, Sb, Bi.

A general idea of the amounts of most of these elements and compounds present in the anode, and of their distribution in solution and residue after electrolysis, is given in Table 116.<sup>4</sup>

The impurities of group I are all electropositive to Cu, and will be therefore dissolved before Cu and concentrated in the electrolyte at the expense of Cu. The first five, Ni, Co, Fe, Mn, and Zn are also attacked chemically by the free  $\text{H}_2\text{SO}_4$  and therefore neutralize it. The Fe goes into solution as  $\text{FeSO}_4$ , is changed into  $\text{Fe}_2(\text{SO}_4)_3$  by anodic oxidation ( $2\text{FeSO}_4 + \text{O} + \text{H}_2\text{SO}_4 = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$ ), and requires an addition of  $\text{H}_2\text{SO}_4$ ; the  $\text{Fe}_2(\text{SO}_4)_3$  formed is again reduced to  $\text{FeSO}_4$  at the cathode by deposited Cu, viz.,  $\text{Cu} + \text{Fe}_2(\text{SO}_4)_3 = \text{CuSO}_4$

<sup>1</sup> Förster-Seidel, *Zt. Electrochem.*, 1897, III, 479.

<sup>2</sup> Rössler, *Dingler Polyt. J.*, 1881, CCXLII, 286.

Wohlwill, in Borchers-McMillan, *op. cit.*, p. 199; *Zt. Electrochem.*, 1903, IX, 311.

<sup>3</sup> Berg, *Hüttenm. Z.*, 1883, XLII, 235, 250, 375, 399, 423; 1885, XLIV, 249, 261, 273.

<sup>4</sup> Keller, *Eng. Min. J.*, 1897, LXIV, 514; *Min. Ind.*, 1898, VII, 239.

TABLE 116.—ANALYSES AND DISTRIBUTIONS OF ANODE IMPURITIES

Element or compound	Example No. 1				Example No. 2			
	Analysis		Distribution in		Analysis		Distribution in	
	Anode, per cent.	Residue, per cent.	Solution, per cent.	Residue, per cent.	Anode, per cent.	Residue, per cent.	Solution, per cent.	Residue, per cent.
Ag.....	0.3432	53.894	.....	100	0.3444	55.150	.....	100
Au.....	0.00173	0.2959	.....	100	.....	0.198	.....	100
Cu.....	99.30	11.010	99.93	0.07	99.40	13.820	99.914	0.086
Pb.....	0.0093	0.910	.....	.....	.....	2.070	.....	.....
Bi.....	0.0320	3.930	21.78	78.22	0.0035	0.340	39.29	60.71
Sb.....	9.0651	6.250	38.86	61.14	0.0510	2.440	70.10	29.90
As.....	0.0586	2.107	77.10	2.290	0.0180	1.090	62.16	37.84
Se.....	0.0025	0.394	.....	100	0.0045	0.718	.....	100
Te.....	0.0075	1.174	.....	100	0.0056	0.892	.....	100
Fe.....	.....	.....	.....	.....	(?)	0.800	.....	.....
SO <sub>4</sub> .....	.....	5.268	.....	.....	.....	10.680	.....	.....
H <sub>2</sub> O (250° C.).....	.....	2.365	.....	.....	.....	2.604	.....	.....

+2FeSO<sub>4</sub>. In general, impurities electropositive to Cu offset its chemical corrosion; they may be present in considerable amounts before they affect the cathode deposit. It has been noticed that if the anode contains much Ni, the residue formed may assay as high as 10 per cent. nickel, the NiO going into the mud, the Ni into the electrolyte.<sup>1</sup>

Lead is converted into PbSO<sub>4</sub> which is practically insoluble and goes wholly into the anode mud.

Tin goes into solution and then falls out as a basic sulphate liberating free acid. It has been noticed that Sn acted favorably upon the smoothness of the cathode copper. This is probably due to its causing the reduction of copper arsenate to arsenite, with which it forms an insoluble compound and thus purifies the bath.<sup>2</sup> At the works of the Chicago Copper Refining Co., the late H. L. Bridgman used to add 25 lb. Sn to 100 tons of Cu in treating copper rich in As; the practice was too expensive for ordinary work. At present the arsenic is eliminated by smelting methods, and no high-arsenic copper is used as anode.

Of the metals in group II, Au and Pt are not dissolved; Ag also is insoluble under normal conditions of electrolyte. Any Ag found in the cathode has been carried to it mechanically. Should the electrolyte become neutral, Ag will be dissolved and deposited. The rare elements Se and Te go completely into the anode mud.

Of the compounds assembled in group III, Cu<sub>2</sub>O is always present in the anode; it is not attacked electrolytically and sinks to the bottom of the vat; there it may be dissolved chemically by the free acid and thus reduce the amount of the latter. The compounds Cu<sub>2</sub>Se, Cu<sub>2</sub>Te, and Cu<sub>2</sub>S are attacked neither electrolytically nor chemically.

<sup>1</sup> L. Addicks, 1912.

<sup>2</sup> Ulke, *Min. Ind.*, 1897, VI, 242;

Peters, "Modern Copper Smelting," 1895, p. 600.



In group IV are collected the three metals which are partly dissolved and which partly fall again out of solution as basic sulphates, or may be deposited with the copper on the cathode. The electromotive force necessary for decomposition is, for Cu 0.30, for As 0.27, for Bi 0.21, for Sb 0.10 volt.<sup>1</sup>

ARSENIC in the metallic state is dissolved as  $\text{As}_2(\text{SO}_4)_3$ , and this salt is more or less decomposed by hydrolysis:  $\text{As}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} \rightleftharpoons 2\text{H}_3\text{AsO}_3 + 3\text{H}_2\text{SO}_4$ , when  $\text{H}_3\text{AsO}_3$  (or  $\text{As}_2\text{O}_3 + \text{aq.}$ ), being only slightly soluble, falls out of solution and goes into the mud. Highly arsenical copper becomes coated with greenish, slimy  $\text{Cu}_3\text{As}_2\text{O}_8$  which increasing the resistance has to be brushed off in case the coating becomes heavy.<sup>2</sup> If with a difference in potential of 0.3 volt, a current density of 15–20 amp. per square foot, and a bath temperature of 40–50° C., the As-content of the electrolyte reaches 2 per cent., As is precipitated upon the cathode; hence the aim is to keep the As-content below 1.25 per cent.

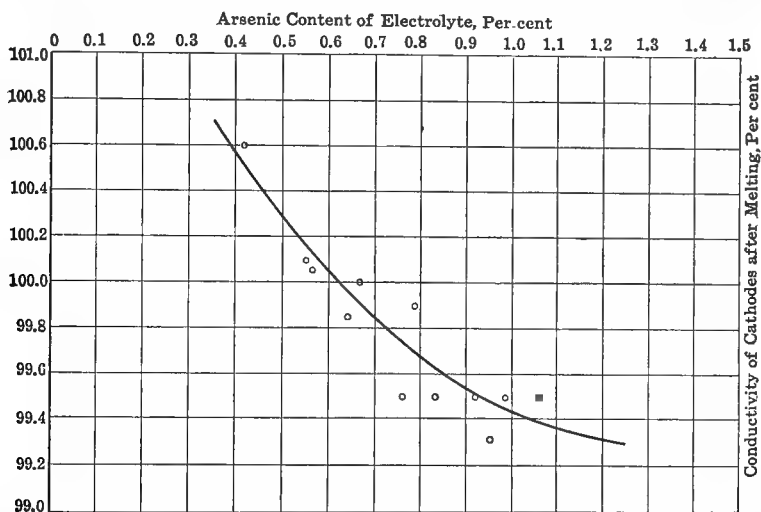


FIG. 483.—Relation of arsenic-content of electrolyte and conductivity of cathode copper (Addicks).

Deposition also takes place when the Cu-content falls below 2.8 per cent. With an anode containing 0.3 per cent. As, from 30 to 35 per cent. of the As goes into the mud, and from 70 to 65 per cent. into the electrolyte. This general figure is changed by the As-content of the electrolyte, as with a bath already containing a considerable amount of As, more of this metal will go into the mud than into the solution. With very small quantities of As, as in refining some Lake copper, all the As goes into the mud. According to Wickes,<sup>3</sup> deposition of As is largely governed by the degree of hydrolyzation.

The relation between As-content of electrolyte and conductivity of cathode-Cu is shown in Fig. 483 (Addicks).

<sup>1</sup> Neumann, *Zt. phys. Chem.*, 1894, XIV, 229.

<sup>2</sup> Ulke, *Min. Ind.*, 1897, VI, 240.

<sup>3</sup> *Tr. A. I. M. E.*, 1905, XXXV, 40

The compound  $\text{Cu}_3\text{As}_2\text{O}_8$  being a non-conductor<sup>1</sup> goes into the mud, where it is in part decomposed by the free  $\text{H}_2\text{SO}_4$  which dissolves the  $\text{As}_2\text{O}_5$ ; some  $\text{As}_2\text{O}_5$  is also formed by oxidation of  $\text{As}_2\text{O}_3$  at the anode.

From a neutral solution As is readily deposited on the cathode.

Wen<sup>2</sup> found that additions of small amounts of  $\text{HCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{AlCl}_3$ , and  $\text{NaCl}$  improved the cathode copper chemically in hindering the deposition of As and Sb, and physically in preventing the formation of trees. Of these inorganic additions,  $\text{NaCl}$  is the most effective.<sup>3</sup> Organic agents, such as gelatine and tannin, aid in furnishing smooth deposits; this is not the case with peptone.<sup>4</sup> The combined addition of 0.01 per cent. Cl in the form of  $\text{NaCl}$ , and of 0.01–0.02 per cent. gelatine gives a smooth ductile deposit of great purity with an electrolyte containing  $\text{CuSO}_4 + 5 \text{ aq.}$ , 15 per cent. and free  $\text{H}_2\text{SO}_4$  10 per cent. held at  $40^\circ \text{C.}$ , even when this contains as much as 6 per cent. As, the current density being 40 amp. per square foot and the pressure about 0.5 volt.

It is common practice to add a very small amount of glue to the storage tank for electrolyte. Even the usual ridiculously small addition decreases the resistance of the bath; further it has been found that it takes a much longer time in the refining furnace to bring such cathodes to the stage of set copper, than if no glue whatever has been used.

**ANTIMONY.**<sup>5</sup>—The behavior of Sb is similar to that of As, but Sb is less readily deposited. In large-scale work some insoluble dark antimony compound is often seen floating on the surface of the electrolyte; there is then danger of its adhering to the cathode and becoming entrapped. Care is usually taken to collect it from the last of a series of vats forming cascades by placing a screen across the outlet or beneath the overflow. The antimony content of the electrolyte appears to remain approximately constant at 0.03 per cent.

The effects of adding organic agents have been noted under arsenic.

**BISMUTH.**—This stands between As and Sb as regards its behavior in electrolysis (p. 487); it is more readily deposited than As. According to Terrill<sup>6</sup> an addition of a drop of Br-water to a sample of electrolyte will indicate by the formation of a white cloud the presence of Bi; if the cloud appears at once, the danger-point of electrodeposition has been reached; if it takes about 1 min. to form, the danger-point will be reached in about 48 hr. Usually Sb, and especially Bi, occur in quantities too small to cause any trouble with the cathode copper.<sup>7</sup>

**251. The Current.**—The efficiency of the refining process is dependent

<sup>1</sup> Johnson, *Electrochem. Ind.*, 1904, II, 207.

<sup>2</sup> Dissertation, Columbia University, 1911; *Tr. Am. Electrochem. Soc.*, 1911, XX, 121.

<sup>3</sup> See also Speer, *op. cit.*, 1912, XXII, 281.

<sup>4</sup> Jarvis, *School Mines Quart.*, 1909, XXX, 100.

<sup>5</sup> Hampe, *Eng. Min. J.*, 1892, LIV, 78; *Berg. Hüttenm. Z.*, 1892, LI, 177; *Chem. Z.*, 1892, XVI, 417.

Sprenst, C. "Das Verhalten von Antimon bei der Kupferraffination," Dissertation, Dresden, 1911.

<sup>6</sup> *Trans. Inst. Min. Met.*, 1897–98, VI, 215.

<sup>7</sup> See also, Motherwell, *Met. Chem. Eng.*, 1913, XI, 670.

upon the character and temperature of the electrolyte, the current density, and voltage.

For a given temperature the conductivities of a  $\text{CuSO}_4$ - and a  $\text{H}_2\text{SO}_4$ -solution increase within certain limits with the  $\text{CuSO}_4$  and  $\text{H}_2\text{SO}_4$  present, but by the addition of  $\text{H}_2\text{SO}_4$  to the  $\text{CuSO}_4$ -solution the dissolving power of the latter for  $\text{CuSO}_4$  is diminished, as well as the dissociation of the salt, *i.e.*, the conductivity of the electrolyte. In the same manner the dissociation of  $\text{H}_2\text{SO}_4$  in the electrolyte is diminished by the presence of  $\text{CuSO}_4$ . Tables 117 and 118 give the experimental results of Richardson and Taylor.<sup>1</sup>

TABLE 117.—CONDUCTIVITIES OF MIXTURES OF  $\text{CuSO}_4+5\text{Aq.}$  AND  $\text{H}_2\text{SO}_4$  IN RECIPROCAL OHMS PER CU.CM.

Temperature	25° C.					45° C.				
Gram $\text{H}_2\text{SO}_4$ in 100 c.c.	0	5	10	15	20	0	5	10	15	20
Gram $\text{CuSO}_4$ +5 aq. in 100 c.c.										
0	.....	0.208	0.410	0.565	0.683	.....	0.246	0.492	0.683	0.839
5	0.953	0.204	0.388	0.531	0.646	0.0205	0.242	0.461	0.643	0.791
10	0.0221	0.195	0.350	0.500	0.600	0.0294	0.222	0.422	0.606	0.738
15	0.0343	0.189	0.338	0.458	0.558	0.0468	0.217	0.381	0.545	0.690
20	0.0423	0.182	0.319	0.433	.....	0.0574	0.212	0.378	0.521	0.643

TABLE 118.—CONVERSION OF DATA IN TABLE 117 TO PRACTICAL NOTATIONS

Gram $\text{CuSO}_4+5\text{aq.}$ in 100 c.c.	Cu, per cent.	$\text{CuSO}_4+5\text{ aq.}$ per cent.	Gram $\text{H}_2\text{SO}_4$ in 100 c.c.	$\text{H}_2\text{SO}_4$ , per cent.
4.0	1	3.91	5.15	5
8.2	2	7.82	10.17	10
17.4	3.99	15.64	16.5	15
27.4	5.99	23.46	22.8	20
32.9	6.98	27.37		

The conductivities of working solutions are about 15 per cent. smaller than those found by the experimental work with mixtures of pure  $\text{CuSO}_4+5\text{ aq.}$  and  $\text{H}_2\text{SO}_4$ .

Table 117 has shown that a rise in temperature of bath increases the conductivity. The relation between voltage and current density in a bath with 16 per cent.  $\text{CuSO}_4+5\text{ aq.}$  (or 4 per cent. Cu) and 9 per cent. free  $\text{H}_2\text{SO}_4$ , for temperatures ranging from 20 to 90° C., is shown in Fig. 484.<sup>2</sup> The voltage does not rise in the same ratio as the amperage, as might be expected, and give a straight-line curve; the curves converge toward the current density axis, and do this the more the lower the temperature of the bath.

The relation between voltage and temperature for different current densities

<sup>1</sup> *Trans. Am. Electrochem. Soc.*, 1911, XX, 179; *Met. Chem. Eng.*, 1911, IX, 536.

<sup>2</sup> Schwab-Baum, *J. phys. Chem.*, 1903, VII, 497.

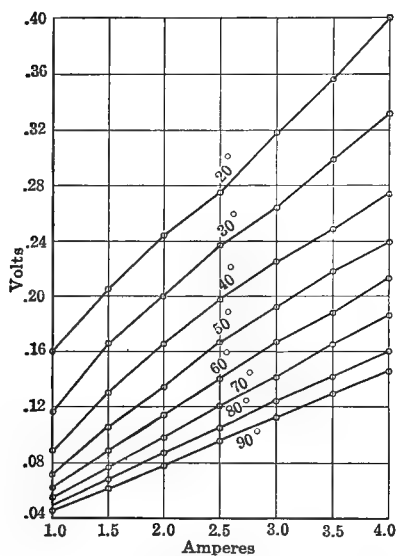


FIG. 484.—Relation of current and temperature in electrolyte with 16 per cent.  $\text{CuSO}_4 + 5\text{aq.}$ , 9 per cent. free  $\text{H}_2\text{SO}_4$ .

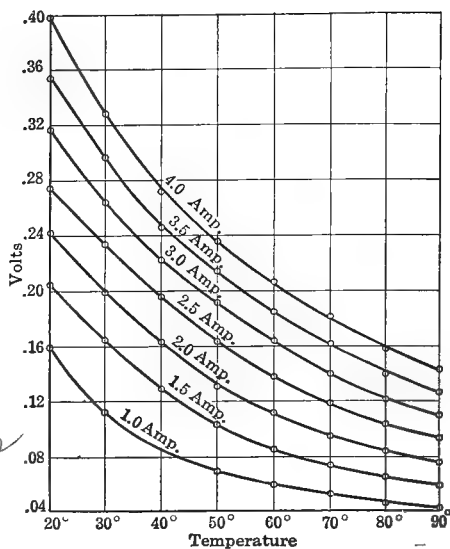


FIG. 485.—Relation of voltage and temperature for different current densities in electrolyte with 16 per cent.  $\text{CuSO}_4 + 5\text{aq.}$ , 9 per cent. free  $\text{H}_2\text{SO}_4$ .

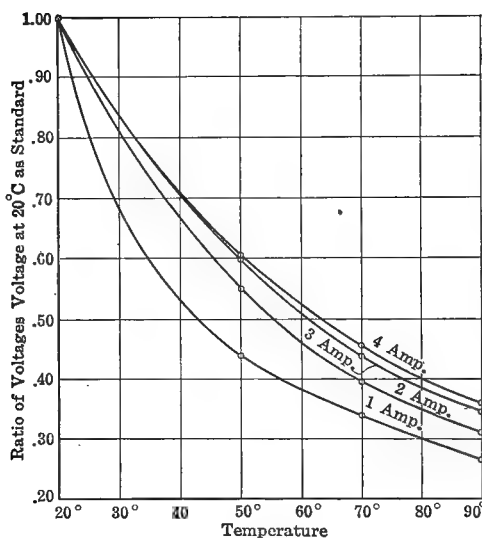


FIG. 486.—Relation of voltage-ratio and temperature for different current-densities in electrolyte with 16 per cent.  $\text{CuSO}_4 + 5\text{aq.}$ , 9 per cent. free  $\text{H}_2\text{SO}_4$ .

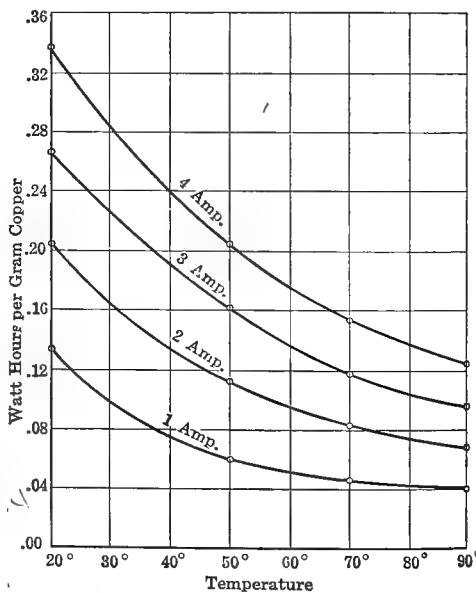


FIG. 487.—Relation of watt-hour and temperature for different current-densities in electrolyte with 16 per cent.  $\text{CuSO}_4 + 5\text{aq.}$ , 9 per cent. free  $\text{H}_2\text{SO}_4$ .

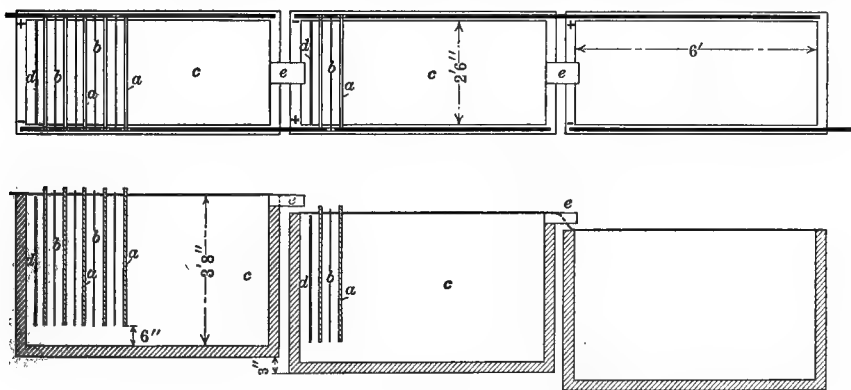
is given in Fig. 485. The voltage, measured with electrodes 1 cm. apart, decreases as the temperature rises; the decrease is rapid at low temperatures, and becomes less and less as the temperature rises.

In order to make the curves in Fig. 485 independent of the electrode distance, the curves in Fig. 486 have been drawn by Schwab and Baum, in which the voltage ratio has been plotted as ordinate instead of the real voltage, voltage at 20° C. having been made the standard. If the voltage at one temperature is known, that for another temperature is found through the curve.

Theoretically 1 amp.-hr. deposits from a  $\text{CuSO}_4$ -solution 1.186 g. Cu, or in order to deposit 1 lb. av. Cu there are required 382.4 amp.-hr. In practice, 400 to 500 amp.-hrs. are necessary. The relation between the watt-hour required for the deposition of 1 g. Cu, and the operating temperature based on the laboratory experiments of Schwab and Baum is given in Fig. 487.

### A. MULTIPLE SYSTEM

**252. The Multiple (Elkington) System in General.**<sup>1</sup>—In this process, Figs. 488–489, the anodes, *a*, of high-grade copper, and cathodes, *b*, of pure copper, are connected in multiple, and suspended crosswise in an oblong vat, *c*, charged with a solution of blue vitriol containing free sulphuric acid. (A current of suitable strength passes from the anodes through electrolyte to cathodes,



FIGS. 488–489.—The multiple system.

dissolves copper from the anodes and deposits it on the cathodes, while insoluble impurities collect on the bottom of the vat as a residue called anode mud or anode

<sup>1</sup> Anaconda: Editor, *Eng. Min. J.*, 1896, LXII, 271. Hering, *Berg. Hüttenm. Z.*, 1893, LI, 54. Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 308. Raritan No. 1: Addicks, *Min. Ind.*, 1900, x, 261 (remodeled in 1912 on lines of No. 2). Balbach S. & R. Co.: *Electrochem. Ind.*, 1904, II, 303 (remodeled 1910). Great Falls: Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 308. Burns, *op. cit.*, 1913, XLVI. Chrome: Addicks, *Min. Ind.*, 1906, xv, 301; *Eng. Min. J.*, 1907, LXXXIII, 1001. Raritan No. 2: Easterbrooks, *Electrochem. Met. Ind.*, 1908, VI, 181, 245, 277. Lithgow, N. S. W.: Blakemore, *Tr. Austral. Inst. Min. Eng.*, 1912, xv, 36; *Eng. Min. J.*, 1910, xc, 717, 769. Port Kembla, N. S. W.: Casey, *Eng. Min. J.*, 1910, xc, 1111.

slime. The deposited copper with its cathode is removed at intervals, melted down in a reverberatory furnace, toughened, and cast into suitable forms. The anode mud containing the electronegative precious metals and insoluble impurities is refined, and cast into bars. Occasionally other substances, such as selenium and palladium, are recovered as by-products; tellurium, for which there is no market at present, goes to waste. The uncorroded part of the anode goes back into the furnace from which the anodes are cast.

**253. Electrolyte—Composition, Temperature, and Circulation.**—The range of composition of the electrolyte is  $\text{CuSO}_4 + 5 \text{ aq.}$ , 12–16 per cent. (= 3–4 per cent. Cu) and free  $\text{H}_2\text{SO}_4$ , 5–13 per cent.; the usual figures are: Cu 3 and free  $\text{H}_2\text{SO}_4$  12 per cent.

The Cu-content is never allowed to fall below  $2\frac{1}{2}$  per cent., as otherwise there is danger of As being plated out; with over 13 per cent. free  $\text{H}_2\text{SO}_4$  the bath is decomposed electrolytically and polarization is likely to offset increased conductivity.<sup>1</sup> In Table 119 are given analyses of electrolytes of different degrees of purity and concentration.

TABLE 119.—ANALYSES OF ELECTROLYTE

	Great Falls, Mont.		Perth Amboy, N. J.		Maurer, N. J.
	Refining Tank	Starting- sheet Tank	Room I	Room II	
Cu.....	3.280	3.404	3.91	4.00	3.1
As.....	0.500	0.425	1.03	1.02	1.0
Sb.....	0.041	0.034	0.009	0.009	0.03
Ni.....	0.377	.....	0.38	0.34	.....
Co.....	0.016	.....	.....	.....	.....
Bi.....	0.021	.....	.....	.....	.....
Fe.....	0.600	0.383	0.096	0.104	0.25
Se.....	None	.....	.....	.....	.....
Te.....	None	.....	.....	.....	.....
Pb.....	Trace	.....	.....	.....	.....
Zn.....	0.418	.....	.....	.....	.....
Ag, Au.....	None	.....	.....	.....	.....
$\text{CaSO}_4$ .....	.....	.....	0.13	0.19	.....
$\text{Na}_2\text{SO}_4$ .....	.....	.....	1.26	0.85	.....
Free $\text{H}_2\text{SO}_4$ .....	13.030	10.213	12.85	12.24	12.0
Total $\text{H}_2\text{SO}_4$ .....	.....	.....	19.73	18.89	.....
Cl.....	0.004	0.0034	.....	.....	0.003
Specific Gravity.....	1.220	1.175	1.255	1.255	1.2
Reference.....	(2)	(2)	(3)	(3)	(4)

The different soluble metal sulphates appear to act cumulatively as regards conductivity, thus, *e.g.*, the conductivity of a bath with 3 per cent. Cu and 0.5 per cent. Ni is approximately the same as one with 3.5 per cent. Cu.

<sup>1</sup> Addicks, "Rapid Measurement of Conductivity," *Electrochem. Ind.*, 1904, II, 306.

<sup>2</sup> Burns, *Tr. A. I. M. E.*, 1913, XLVI.

<sup>3</sup> Private Communication, C. H. Aldrich.

<sup>4</sup> Private Communication, H. H. Alexander.

In working, the normal composition of the bath is likely to be changed. It is impoverished in Cu because the electropositive metals Zn, Fe, Ni, Co, and Mn go into solution and replace equivalent amounts of Cu; it is enriched in Cu by the chemical action of the free  $\text{H}_2\text{SO}_4$  and by the dissolving effect of  $\text{CuSO}_4$  upon Cu (§ 243), which takes place largely at the surface of the bath; the total amounts to from 0.5 to 1 per cent. of the Cu deposited. With the high-grade anode in common use at present, any impoverishment in Cu is more than balanced by enrichment; hence Cu is removed at intervals either in the metallic state, by plating out, or as blue vitriol by crystallizing out. In general from 1 to 2 per cent. of the cathode capacity has to be removed. However, in the presence of much Fe and Ni, more Cu may be deposited than is dissolved. The electrolyte is always impoverished in its content of free  $\text{H}_2\text{SO}_4$  because the separation of impurities as normal or basic sulphates, and to the chemical action of the free  $\text{H}_2\text{SO}_4$  upon Cu and  $\text{Cu}_2\text{O}$ . The acid has therefore to be replenished.

The temperature of the bath ranges from 40 to 60° C. The hotter the bath, the lower the resistance and the smoother the cathode deposit, but the chemical action of the acid is also greater. The electric energy raises the temperature to about 34° C.; for a higher temperature heating by steam-coils (1-2 in. in diameter) in storage tanks is required. With 60° C. the evaporation in 24 hr. in a tank is about 22 lb. water per square foot solution exposed. The fall in temperature of the electrolyte in passing through a cascade is about 5° C. in summer, and 10° C. in winter. The idea of covering tanks<sup>1</sup> to diminish the reduction of temperature owing to radiation is at present impracticable.<sup>2</sup> Experiments are, however, under way to make it practicable.

Continuous circulation is essential to correct differences in composition of electrolyte caused by the process. At the anodes, where copper goes into solution, the electrolyte is heavier than at the cathodes, where it goes out of solution; the heavier part sinks and the lighter rises, causing layering in the bath; the current passing mainly through the heavier solution causes uneven corrosion of the anode and irregular deposition on the cathode. The greater the current density and the higher the temperature of the bath, the more rapid the circulation required. Thus, with a current density of 40 amp. per square foot of cathode area, the electrolyte is exchanged once in 3 hr.; with 15 amp. once in 4 hr., with 10 amp. once in 5 or 6 hr., the rate of flow ranges from 6 to 3 gal. per minute.<sup>3</sup> It is important that the flow be sufficiently slow to permit all anode residue to settle, and its path in such a direction as to leave settled residue undisturbed. The rate of circulation is also governed by the impurity and precious metal of the anode. Thus, the higher the As-content the greater has to be the rate of circulation, if the deposition of As is to be avoided; on the other hand the higher the content in precious metal, the slower has to be the

<sup>1</sup> Schwab-Baum, *Jl. Phys. Chem.*, 1903, VII, 493.

<sup>2</sup> Addicks, *Electrochem. Ind.*, 1903, I, 487.

<sup>3</sup> Tests at Great Falls by Burns, *Tr. A. I. M. E.*, 1913, XLVI.

circulation in order to prevent stirring up the large amount of mud which settles on the bottom of the vat.

Kiliani<sup>1</sup> measured the differences in potential arising when working with and without circulation.

The usual method of circulation is to have rows of vats on wide terraces with steps 2-3 in. high, and to let the electrolyte overflow from the vats on the top row into those on the next row below and so on. In Fig. 490 the electrolyte is raised from a well into a main whence one part flows into a distributing box for the electrolyzing vats arranged on either side in cascades, while another is diverted to the liberators, *i.e.*, vats with insoluble anodes in which electrolyte is freed from Cu, As, etc., and then returned as fresh acid to the main circuit. From the last row of electrolyzing vats the electrolyte flows into a trough emptying into the well or sump connected with the pump. Each of the vats in Fig. 490, as well as in Figs. 505-506 (Great Falls, Mont.).

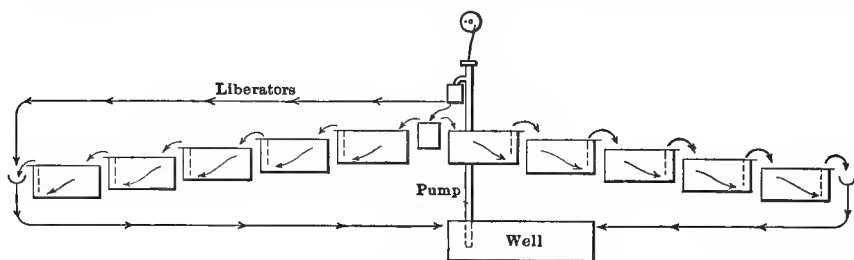


FIG. 490.—Circulation of electrolyte.

shows a partition at the discharge-end which reaches to within 6 or 8 in. from the bottom so as to leave room for the settling of the anode mud. The electrolyte is received on the top of the bath at one end, and withdrawn from near the bottom at the other; it thus has to travel diagonally through the vat whereby a uniform density is maintained.<sup>2</sup> Another arrangement, Figs. 488-489, is to have the partition, *d*, at the feed-end; when the electrolyte is delivered back of the partition, sinks downward and travels diagonally upward to the discharge spout, *e*, at the delivery end.

The arrangement at the Raritan plant No. 2, Perth Amboy, N. J., is shown in Fig. 491. The electrolyte is delivered to a tank back of a semicircular lead partition at the inflow-side and passes to the bottom; the bulk of it overflows at the top at the opposite end, but a small amount of heavier solution is withdrawn near the bottom through three rows of small holes in the lead partition. Attention may be called in connection with Fig. 491 to the means employed for preventing any countercurrent or stray electric current from interfering with the main current. The delivery and receiving mains rest

<sup>1</sup> *Berg. Hüttenm. Z.*, 1885, XLIV, 273.

<sup>2</sup> Inefficiency of method with high current density at Great Falls; Burns, *Tr. A. I. M. E.*, 1913, XLVI.



upon glass; the branch delivery and receiving lead pipes are cut and connected by non-conducting hose, and are protected by vitrified brick.

If the tanks are all on one level they may either receive their solutions severally from a common feed-trough, as was the case with the original plant

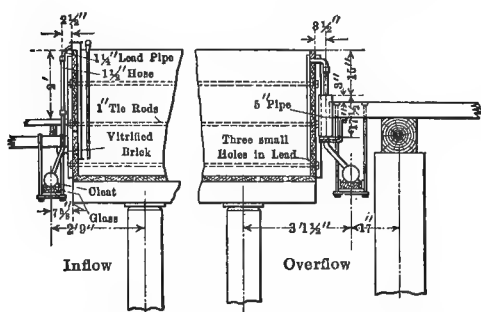


FIG. 491.—Circulation of Electrolyte at Raritan Plant No. 2.

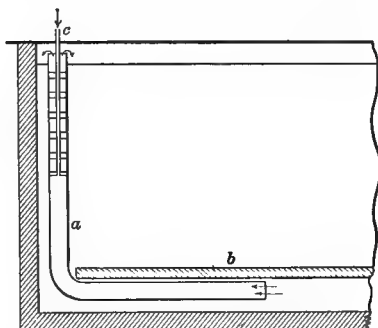


FIG. 492.—Siemens-Borchers circulation of electrolyte.

of Great Falls, Mont.,<sup>1</sup> and deliver into a common discharge trough, or the solution of each tank may be circulated independently by the Siemens-Borchers apparatus<sup>2</sup> sketched in Fig. 492. An L-shaped lead pipe, *a*, is lowered at one end of the vat so that the horizontal arm shall lie on the bottom and underneath

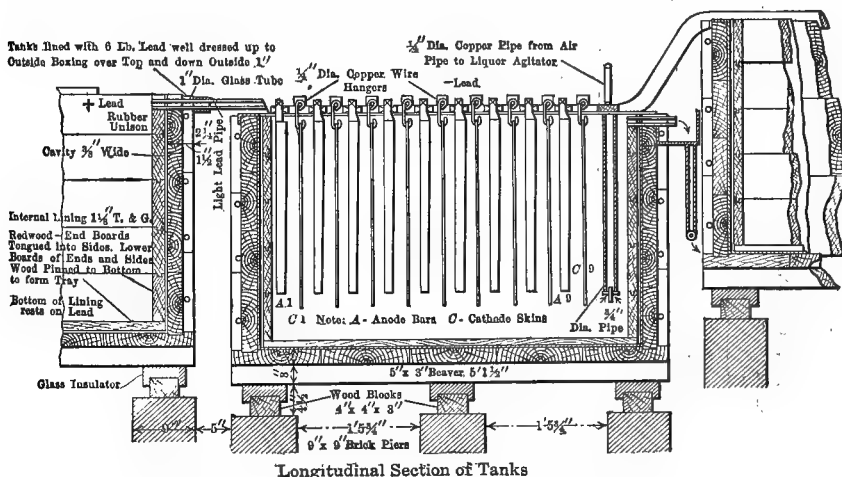


FIG. 403.—Circulation of electrolyte at Lithgow, N. S. W.

the tray, *b*, which is to receive the anode mud. A smaller lead tube, *c*, drawn down at the bottom, is inserted into the vertical arm. Air under 3 or 4 lb. pressure is forced down tube *c*, rises between *a* and *c*, acts as an air-lift pump, and causes the solution to overflow from pipe *a*; a corresponding amount of

<sup>1</sup> Burns, *Tr. A. I. M. E.*, 1913, XLVI.

<sup>2</sup> Borchers-McMillan, *op. cit.*, p. 221; *Zt. Electrochemie*, 1904, p. 221.

course must enter at the bottom. In this manner the solution of each vat is circulated independently of its neighbor, and at the same time aërated. The aëration of warm solution will cause ferrous salt to be converted into insoluble basic ferric salt, and the electrolyte to become purified. (Schneider-Szontag<sup>1</sup> slightly modified the above device at Maurer, N. J. The rate of circulation by

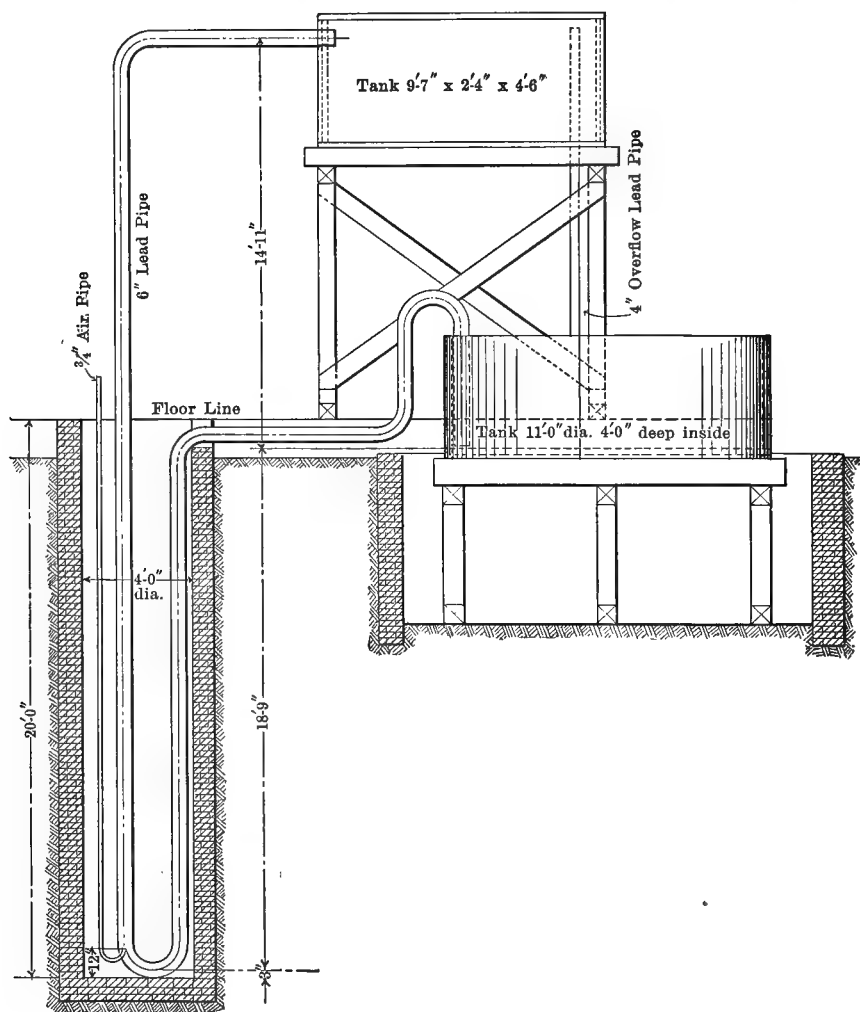


FIG. 494.—Pohlé air-lift pump, Great Falls, Mont.

the apparatus is not sufficiently large for the current density used in the United States, and the method has therefore been given up.)

A modification is in operation at Lithgow, N. S. W.,<sup>2</sup> where a vertical  $\frac{1}{4}$ -in.

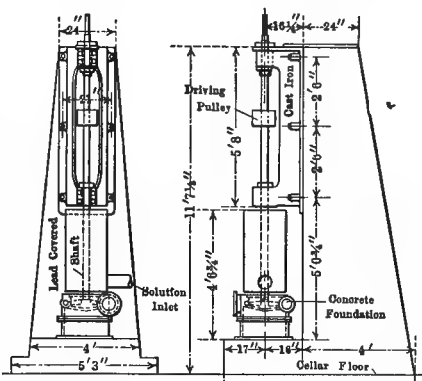
<sup>1</sup> Ulke, *Eng. Min. J.*, 1896, LXII, 464.

<sup>2</sup> *Tr. Aust. Inst. Min. Eng.*, 1912, xv, 36; *Eng. Min. J.*, 1910, xc., 717.

copper pipe connected with air under 5 lb. pressure at the upper end and turned up at the lower, discharges into the lower end of a  $\frac{3}{4}$ -in. vertical lead pipe reaching to within 6 in. from the bottom of the tank; the compressed air acts as a Pohlé air-lift pump and raises the bottom part of the solution to the top; this is done in addition to the regular circulation of the electrolyte down the cascade. The fall in temperature of a bath varies with the size of vat, and the rate of circulation, which in its turn is dependent upon the current density. As shown on page 493 the range of temperature is from 5 to 10° C., varying with the season of the year.

The electrolyte from the lowest numbers of the cascades is collected in a sump and pumped into a distributing tank. Formerly lead-lined acid-eggs and plunger pumps were used for this purpose; at present the Pohlé air-lift pump<sup>1</sup> and the Antisell centrifugal pump have replaced the older apparatus.

The Pohlé air-lift pump in use at Great Falls, Mont., is shown in vertical section in Fig. 494. The feed and delivery pipes, connected by a return-bend, are 6 in. inside diameter, have  $\frac{3}{4}$ -in. walls of hard lead, are cast in 4-ft. lengths with flanges (the air-pipe is  $\frac{3}{4}$  in.); the whole is held in a cement-lined well, 18 ft. 9 in. deep and 4 ft. in diameter. Working against a head of 14 ft. 8 in., 160 gal. electrolyte (specific gravity 1.22) are raised per minute with 80 cu. ft. free air of 16 lb. pressure.



FIGS. 495-496.—Antisell circulating pumps, Raritan Works.

The Antisell centrifugal pump, Figs. 495 and 496, of the Raritan Copper Co., Perth Amboy, has a hard-lead (12 per cent. Sb) cylinder, 4 ft. 6 $\frac{3}{4}$  in. high and 14 in. in diameter, above which are the bearings of the driving shaft carrying at its lower end the rotor making 750 r.p.m. The inlet and outlet pipes are 8 in. in diameter. The pump handles 46.5 cu. ft. solution per minute, has a capacity of 66 cu. ft., and requires 5 h.p.

**254. The Current.**—The drop in potential between vats ranges from 0.2 to 0.4 volt. Magnus<sup>2</sup> found at Anaconda that of this total fall as much as 22.5 per cent. was due to contact resistances and current leakages. At Great Falls, Mont.,<sup>3</sup> the drop between anode busbar and anode is 7.40 per cent. of total voltage, between cathode busbar and cathode 9.24 per cent., and across the electrolyte 83.36 per cent. Addicks<sup>4</sup> distributes the resistances in a tank as

<sup>1</sup> Hofman, "General Metallurgy," 1913, p. 710.

<sup>2</sup> *Electrochem. Ind.*, 1903, 1, 561.

<sup>3</sup> Burns, *loc. cit.*

<sup>4</sup> *Jl. Franklin Inst.*, 1905, CLX, 431; Private Comm., 1912.

See also Hutchinson, *Electrochem. Ind.*, 1904, II, 13, Addicks, *op. cit.*, p. 180; Spalding, *Min. World*, 1910, XXXII, 102 (Power).

follows: metallic 10 per cent., liquid 60, transfer 5, contact 15, counter 5, slime 5. With well-insulated tanks and broken connections in circulating pipes, the current shunted around by grounds should not exceed 1 per cent. of this total; short-circuits between anodes and cathodes or by indirect contacts between electrodes and tank-walls amount to  $5 \pm$  per cent.; hence the efficiency shows a range of 90 to 95 per cent. It is essential to keep contacts bright by scouring with emery; the bright surfaces are sometimes coated lightly with oil to retard corrosion.

The current density shows a range of 12 amp. per square foot (Calumet & Hecla) to 34 amp. (Great Falls);<sup>1</sup> the former average of Eastern refineries of 15 amp. has been raised to 18 to 20 and 21. The low current density at the Calumet & Hecla refinery is due to the desire of preventing even a trace of As in the anode from passing to the cathode.<sup>2</sup> The high density of Great Falls finds its explanation in the cheap water-power of the Missouri River which compensates by the large output for the given plant for the loss of energy. With a large density it is necessary to exchange the cathodes more frequently than with a low in order to prevent short-circuiting. Thus at Great Falls, in 1904, with 40 amp., exchanging cathodes every second day gave an ampere efficiency of 91 per cent., while with four-day cathodes this fell to 85 per cent.

The more recent data by Burns,<sup>3</sup> dealing with current densities of 32.6–36.9 amp. per square foot, are given in Table 120.

TABLE 120.—RELATION OF AGE OF CATHODES AND NUMBER OF ELECTRODES IN TANK

Age of cathodes, days	Electrodes per tank		Average amperes	Av. amperes per sq.ft	Ampere efficiency, per cent.	Cu per kw-hr., lb.	Cathode, oz. Ag per ton	Cathode, per cent. As+Sb
	Anodes <sup>4</sup>	Cathodes						
4	20	20	9,300	36.9	88.0	3.93	1.32	0.0036
2	20	20	8,808	35.0	90.85	3.72	0.83	0.0030
3	20	20	8,878	35.2	89.00	3.75	0.83	0.0032
2	21	21	9,035	34.1	90.90	3.84	0.89	0.0032
3	21	21	9,223	34.8	89.40	3.87	1.02	0.0029
2	22	22	9,071	32.6	90.50	4.02	0.89	0.0033
3	22	22	9,167	33.0	88.80	4.07	0.95	0.0030

With a density of 15 to 20 amp., two cathodes serve for one anode; with 10–12 amp., they are exchanged only when the corroded anode is ready to be removed.

Large plants are divided into several sections, each of which is served by one generator. Numerical examples are shown in Table 128, where details are given with the descriptions (§ 266) of the Anaconda, Great Falls, and Raritan No. 2 plants.

<sup>1</sup> Forty amp. in 1904.

<sup>2</sup> It is the intention to raise the density.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> Converter anodes: Cu 99.13, As 0.127, Sb 0.055 per cent.; Ag 33.91 and Au 0.22 oz. per ton.

**255. Anode.**—The anode ought to be of such a character that it is evenly corroded and does not affect the cathode deposit. Even corrosion is possible only if the amount of impurity present is small and the pitch of the copper right. An anode rich in precious metals usually assays 97.5 per cent. Cu; one with little silver, 99 per cent. Cu and over; 95 per cent. Cu is probably the lowest permissible figure. Analyses of anodes are given in Table 120.

TABLE 120.—ANALYSES OF COPPER ANODES<sup>1</sup>

	Range, U. S.	Average, U. S.	Kosaka, Japan	Maurer, N. J.	Great Falls, Mont.	Raritan, Perth Amboy, N. J.	
Cu.....	98-99.5	99.25	99.034	.....	99.1300	98.986	99.5741
Ag oz.....	0-300	{ incl. in. Cu	42.19	300	39.98	90.00	75.00
Au oz.....	0-40		0.4509	.....	0.23	1.25	0.60
As.....	0-2	0.05	0.044	0.08-0.15	0.1183	0.196	0.048
Sb.....		0.05	0.065	.....	0.0534	0.017	0.018
Bi.....		0.01	0.049	.....	0.0038	0.014	0.0055
Fe.....		0.01	0.004	0.03	0.0110	0.047	0.019
Ni.....		0.08	.....	.....	0.0420	0.093	0.021
Co.....		.....	.....	.....	0.0018	.....	.....
S.....		0.003	0.009	.....	0.2610	0.177	.....
Se.....		0.03	.....	some	0.0090	0.006	0.011
Te.....		0.03	.....	some	0.0170	0.014	0.013
Si.....		0.05	.....	.....	.....	.....	.....
Pb.....		0.02	0.109	.....	0.0065	0.140	0.013
Zn.....		0.01	0.001	.....	0.0035	.....	.....
Reference	Addicks, <i>Jl. Franklin</i> <i>Instit.</i> , 1905, clx, 422.	Addicks, private communi- cation, 1912	Private communi- cation, 1910	Private communi- cation, 1912	Burns, <i>Tr.</i> <i>A. I. M. E.</i> , 1913, xlvi	Private communica- tion, 1912	

If an excess of harmful impurity is present in any shipment, it is good policy to mix this with material of higher grade from another source in the casting furnace instead of running chances of over-charging the electrolyte with harmful metal and obtaining inferior cathode copper.

In the United States most of the anode material is converter copper, hence high-grade, and low in As, say 0.05-0.10 per cent. Formerly with reverberatory copper the As-content frequently exceeded 1 per cent.

Anodes cast direct from the converter are less desirable than after the copper has been transferred to a reverberatory furnace and poled to reduce the O- and SO<sub>2</sub>-content, as the anode is irregular in thickness calling for wide spacing in the tank, is unevenly corroded, gives much scrap, and furnishes an anode mud rich in Cu. Thus experiments at Great Falls, Mont.,<sup>2</sup> showed that converter copper with Cu 99.27 and As, Sb 0.071 per cent., Ag 61.14 and Au 0.20 oz. per ton, gave 8 per cent. scrap, screened (40-mesh) mud with Cu 40.3 per cent., Ag 67.55 and Au 18.34 oz. per ton, and cathodes with 1.25 oz. Ag per ton;

<sup>1</sup> See also p. 486.

<sup>2</sup> Hofman, *Tr. A. I. M. E.*, 1904, xxxiv, 310; Burns, *op. cit.*, 1913, XLVI.

while similar copper with Cu 99.27, As, Sb 0.071 per cent., Ag 61.14 and Au 0.219 oz. per ton poled in the reverberatory furnace gave 5.30 per cent. scrap, mud with Cu 18.80 per cent., Ag 14079 and Au 38.45 oz. per ton and cathodes assaying 0.95 oz. per ton. If, nevertheless, anodes are frequently cast direct from the converter, the reason is that saving the expense of the work in the

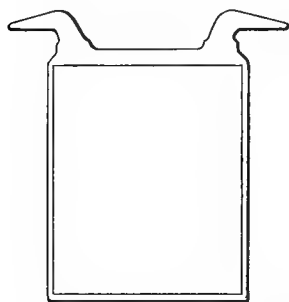
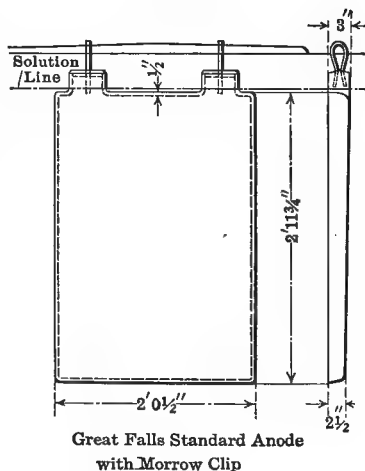


FIG. 497.—Anode with shoulder.

reverberatory furnace more than balances the disadvantages of a higher percentage of scrap, of a greater cost of treating the mud, and of the loss of Ag in the cathode copper. In preparing anode material in the refining furnace, the poling is carried only to plate-pitch, *i.e.*, the cast plate shall have a level surface, and for this the copper must retain a considerable amount of  $\text{Cu}_2\text{O}$ .

The size of the anode is largely determined by the convenience of handling. At first, anodes were made small, 30×24 in. and 1 in. thick, and weighed about 230 lb. They were raised and lowered singly by a block and tackle suspended from an overhead track. At present, they are usually larger, about 3 ft. square, owing to the fact that the twenty odd anodes of a vat are raised and lowered together by means of an overhead electric traveling crane. The width of the anode is limited in part by the tendency of the opposing cathode to curl before it has thickened sufficiently to become rigid. In fact, a new cathode is usually removed after it has been in the vat for two days, straightened in order to make the electrode-distance uniform, and lowered again in place. This curling can be avoided by using two cathodes for one anode as was done at Anaconda, Figs. 530–534, and is still the custom at the Balbach works, but this complicates the handling by means of a crane. The length may be influenced by the percentage of precious metal present, as the lower end of the cathode is likely to become richer in Ag than the upper because of contamination with falling slime. Anodes containing much precious metal will be made shorter than those containing little; the other remedy, deepening of tank, means a larger crane-lift.

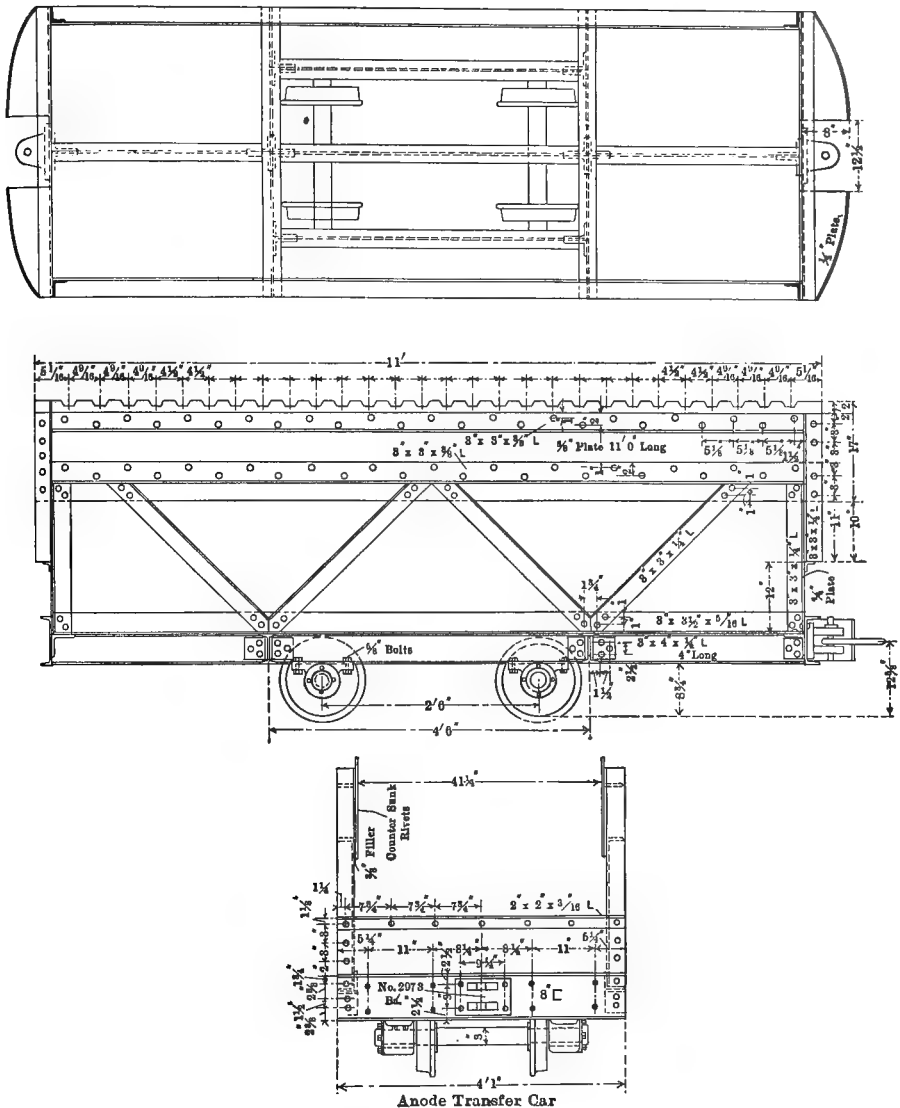


FIGS. 498–499.

The anode situated near the bottom-outlet of the electrolyte, Figs. 505–506, is sometimes made shorter than the rest, to counteract any stirring-up of settled slime.

The thickness depends again upon the amount of precious metal as well as upon the cost of handling. A thick anode takes a long time for corrosion and

represents a large average for tank resistance, but requires only a single handling; a thin anode furnishes a large percentage of scrap to be resmelted because of the disproportionate weight of the supporting lugs. An anode is expected



FIGS. 500-502.—Transfer-car for anodes.

to be corroded in from two to six weeks, and is made from 1 to 1.5 in. thick. Details of some anodes are given in Table 128.

The manner of suspension and with it the form of the upper part of the anode varies at different works. Ordinarily the anode is cast with a projection or

arm or lug on either side, as in Fig. 497, representing the Anaconda anode, by which it rests on the conductor bars. (Sometimes it is cast with two perforated lugs, Figs. 530-534, by means of which it is suspended with heavy copper-wire hooks from the cross-bars.) A third method is represented by the one using the Morrow clip, Figs. 498-499, found at Great Falls, Mont., and Maurer, N. J., a loop of  $\frac{1}{4}$ -in. copper rod the ends of which are placed in the anode mold before filling with copper. The electric contact is thus made perfect.

Each form has its defenders; the main consideration, besides perfection of electric contact, is to reduce as much as possible the amount of metal not immersed in the electrolyte, which has to go back to the anode furnace. At Great Falls<sup>1</sup> with the anode shown in Figs. 498-499, and weighing 500 lb., the scrap formed in 1912 was 5.9 per cent.

The manner of casting has undergone many changes. At first, the open cast-iron anode molds placed on the floor were filled by hand-ladles;<sup>2</sup> later suspended (bull) ladles came into use, and these are still common in plants dealing with charges of 30 tons of copper and less; for some time the metal was tapped into sand molds. The advent of the Walker casting-machine, Figs. 425-426, which permitted reverberatory-furnace charges of 200+ tons of copper, did away with ladling in large plants. Forms of rotating tables other than the Walker or Clark are in use at Great Falls (Kleppinger machine, Figs. 353-354) and Brooklyn; link-belt machines (p. 400) are found at Perth Amboy and Chrome, N. J., and Anaconda, Mont. Special attention has been given to the details of the molds to prolong the life, to insure a smooth bearing surface of the arm, and to obtain an easy release of the anode. An anode is released from the mold either by a knock-out pin (p. 400) raised mechanically from the center of the mold, or by prying after having removed near the top a detachable part of the rim of the mold. A released anode is picked up by a compressed-air lifting apparatus and lowered in an iron water-tank the sides of which have notches to receive the shoulders of the anodes. A tank is of the same size as a depositing vat, and the distance between the notches is equal to the electrode distance. The anodes are cooled and scaled, *i.e.*, freed from  $\text{Cu}_2\text{O}$ , by the immersion. From the immersion tank the anodes are removed by an overhead electric crane and deposited on a transfer car, Figs. 500-502, on which they are hauled to the tank room.

The anode molds used are always open. Truswell has developed a closed mold.<sup>3</sup>

**256. Cathode.**—The cathode, or starting sheet, is a thin plate of copper deposited upon rolled sheet copper,  $\frac{1}{8}$ – $\frac{1}{4}$  in. thick, in a special set of “stripping tanks” which usually are made deeper than the regular corroding tanks. Figs. 503-504 show such a “stripping sheet” riveted to a pair of cross-bars. In order to prevent the deposited metal from adhering to the rolled sheet, the latter is

<sup>1</sup> Burns, *loc. cit.*

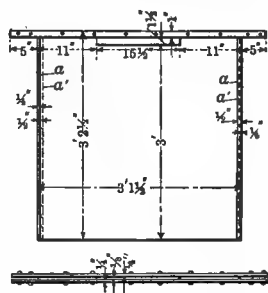
<sup>2</sup> Illustration, *Min. Sc. Press.*, 1899, LXXIX, 266.

<sup>3</sup> *Eng. Min. J.*, 1906, LXXXI, 853.



greased and then sprinkled from a pepper-box with well-conducting graphite or painted with a low-grade mineral oil containing artificial graphite, 1 gal. oil: 0.5 lb. graphite. Ordinarily the rim of the rolled sheet is coated for the width of 1 in. with asphalt in order to prevent the plating-out of any copper and thus facilitate the stripping of the deposited copper when this has reached a thickness of about  $\frac{1}{8}$  in. The coating of asphalt is applied with a brush, or the sheet is dipped. Sometimes grooved strips of wood slipped over the sheet take the place of the asphalt. Instead of giving the sheet copper approximately the shape of the starting cathode, a small groove,  $\frac{1}{8}$  in. deep, is made in the stripping sheet,  $\frac{1}{4}$  in. from the rim,  $a-a$  on one side and  $a'-a'$  on the other in Fig. 503, which traces the outline of the starting cathode; then the sheet is greased, peppered, and suspended in a corroding vat supplied with the regular anodes. The deposited copper will part readily along the groove when the plated metal is being removed. This makes the stripping, first of the metal and then of the border by means of a chisel-pointed bar, easy, and the starting cathodes are well trimmed at the same time. According to Huntington<sup>1</sup> the lines of crystallization of deposited metal are at right angles to the surfaces on which the deposit is made; hence in a groove there will be discontinuity of the two sets of crystals and a line of weakness will be developed, a phenomenon resembling the line of weakness in a rectangular casting in which the crystals arrange and group themselves with their principal axes in lines perpendicular to the cooling surfaces.<sup>2</sup>

In order to give the thin starting cathodes the tensile strength<sup>3</sup> necessary to carry the weight of the copper to be deposited, it is important that the copper be plated out slowly; hence the current density is made lower than in regular work, e.g., one-half at Great Falls. This is accomplished by dividing the current, and by increasing the resistance of the electrolyte, either by reducing the copper and acid-content or by adding gelatine to the bath. The ampere efficiency is about 85 per cent.<sup>4</sup> There is provided one starting sheet tank for 6 to 12 corroding tanks. The time required for preparing a starting cathode of a given thickness is ascertained from the fact that 1 amp. per square inch (or 144 amp. per square foot) will give in 1 hr. a deposit 0.008104 in. thick. Ordinarily it takes 10 days to prepare a sheet; at Great Falls the time is 12 hr. The cathode is usually made slightly longer and wider than the anode, Figs. 505-506, in order to prevent or diminish the formation of excrescences. The cathode extends downward to 6 or 8 in. from the bottom of the tank, in order to leave room for the accumulation of anode mud and for the passage of the



FIGS. 503-504.—Cathode stripping-sheet.

<sup>1</sup> *Eng. Min. J.*, 1905, LXXX, 1109, photomicrographs.

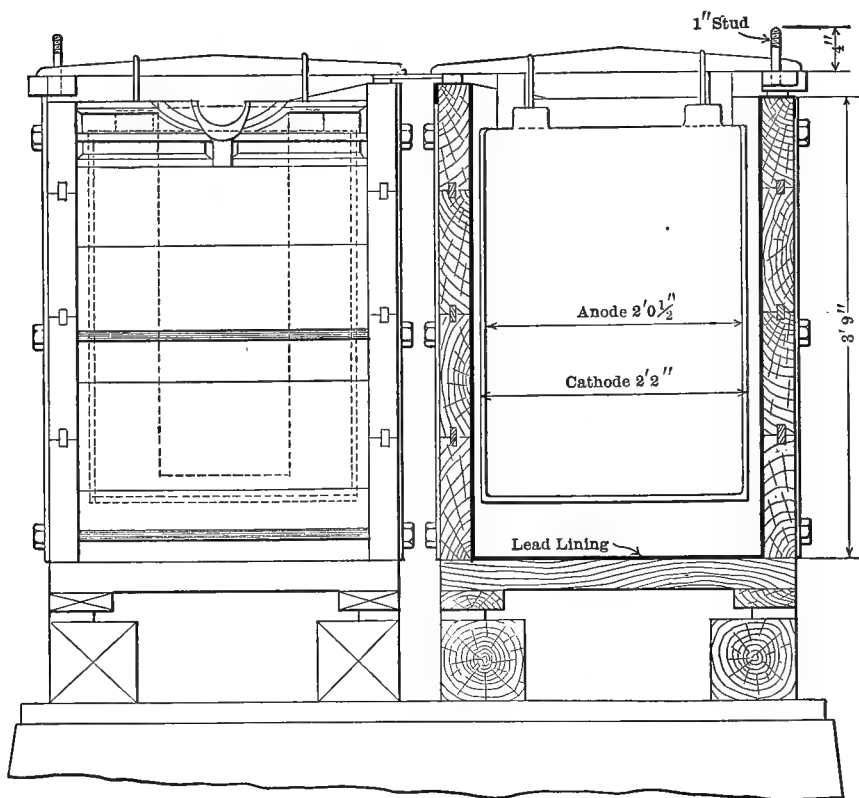
<sup>2</sup> Microphotographs of Wäser and Kühnel, *Electrochem. Zt.*, 1912, XVIII, 151, 211.

<sup>3</sup> Förster, *Berg. Hüttenm. Z.*, 1899, LVIII, 473.

<sup>4</sup> Table by, Burns, *loc. cit.*

electrolyte; it is about 2 in. narrower than the tank and furnishes a 1-in. space on either side for the electrolyte.

The form of the upper part of a starting cathode depends upon the manner in which it is suspended from its cross-bar. This is always of copper, usually 1 in. in diameter and flattened at the ends to furnish the necessary contact surface. Formerly the cathode was a rectangular sheet of which one end was bent 180° C. and hooked on the bar; at present there are usually two strip-like extensions at the suspension end, as shown in Fig. 507, by means of which the



FIGS. 505-506.—Tank details of Great Falls.

cathode is connected with the cross-bar.) Ordinarily the strips are made sufficiently long to serve as flat hooks after having been bent 180°. At Anaconda, Figs. 530-534, the upper rim of the small (11×33 in.) starting sheet used to be bent and clamped over the ends of a loop of sheet copper, 11×4.5 in., by a machine similar to one used in making stove-pipe. At Great Falls and Perth Amboy (Raritan No. 2), the Morrow clip, Figs. 508-509, is in use: a loop of deposited copper is fastened to the starting sheet by a machine which on one side punches a hole through the loop and sheet, bends over the protruding ends at the opposite side and forces them down. At Maurer, N. J., two holes

are punched through loop and sheet to insure against accident. Whatever may be the manner in which the starting cathodes are suspended, care must be taken to have them straight before they go into an electrolyzing vat; after having been in a vat for two days they are taken out singly, placed on an inclined wooden plane, held on a movable wooden support, and straightened with suitable wooden beaters.

The cathodes of a tank are removed together by means of an overhead electric crane after seven to fourteen days, dipped into hot water, and then de-

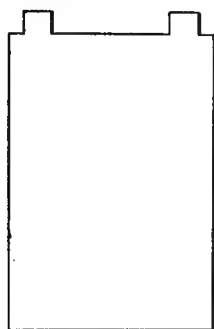
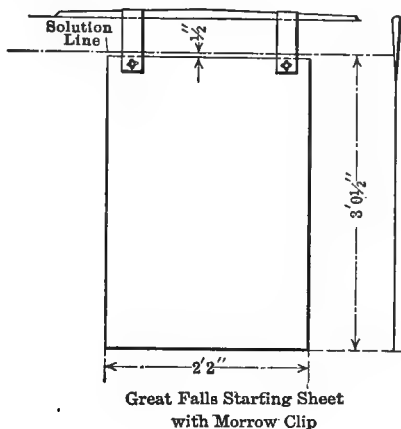


FIG. 507.—Starting-sheet with extensions to be bent over.



FIGS. 508-509.

posited on a transfer car to go to the refining furnace to be melted, fire-refined, and cast. The cast copper generally shows an electric conductivity lower by 1 to 1.5 per cent. in comparison with the cathode copper.<sup>1</sup> This is due to occluded electrolyte and anode mud, and to the absorption of impurity (S) from the furnace fire-gases.

**257.—Manipulation of Electrodes.**<sup>2</sup>—An electrolyzing vat holds at present 20+ anodes and one cathode in excess of the number of anodes; as many as 60 electrodes are permissible. Formerly each electrode was handled by itself; at present the anodes of the vat are charged and removed together, as well as the cathodes. Thus, as already indicated, the anodes for a tank are stacked upright on a skeleton transfer car, Figs. 500-502, which is hauled by horses, steam, or electric locomotives to the tank house. Here they are raised together by an overhead electric traveling crane, transferred to the tank for which they are intended, and lowered. The remains of the corroded anodes of a tank are removed in the same way, transferred to a washing tank where they are brushed to free them from anode mud, and removed to the anode furnace room.

The starting sheets, prepared in a division of the tank house, are also stacked,

<sup>1</sup> Emrich, *Tr. A. I. M. E.*, 1912, XLIII, 453.

<sup>2</sup> Editor, *Eng. Min. J.*, 1911, XCII, 50.

taken by the crane, and lowered in the vats. The finished cathodes are handled similarly. At Great Falls the cathodes are first dipped into water and drained, then 30 per cent. of the sheets making up a charge are dipped into milk of lime and allowed to dry. The coat of lime protects the plates from the sulphur in the fire-gases while melting.

The ELECTRODE DISTANCE is usually about 2 in.; the fall in potential between a pair placed in series is about 0.3 volt. Extremes in electrode distance are 1.5 and 2.5 in., the larger figure will be found with anodes that are impure or that run high in precious metal. If the distance is too small, fragments of copper, anode mud, excrescent growths, etc., tend to bridge the space and cause short-circuiting; if it is too large, there is an unnecessary increase in resistance, less copper is deposited, and electric energy is lost by being converted into heat.

**258. Depositing Vat.**—Formerly the depositing vats were arranged in single rows, Figs. 488–489. (The vats, Fig. 510, were built almost universally of 3-in.

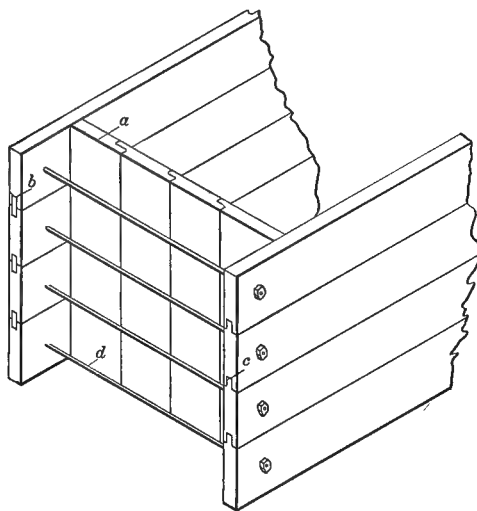


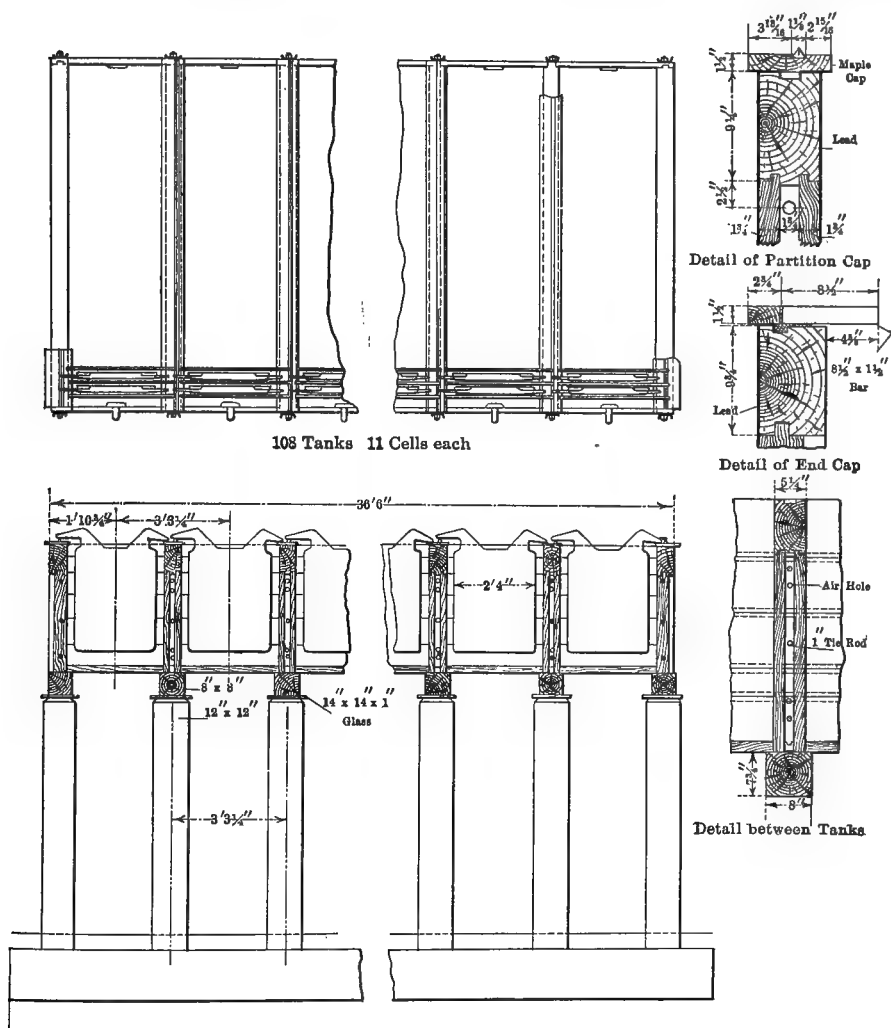
FIG. 510.—Depositing vat.

planks connected by rabbet, *a*, tongue and groove, *b*, or feather, *c*, joints; threaded tie-rods, *d*, passed at the ends through the projecting side planks, Figs. 505–506. This method is still common with vats that stand isolated. Sometimes the vats used to be coated with asphalt, rubber, or some other impervious paint; but more generally they were, and are to-day, lined with 6- or 8-lb. lead which extends over the top, Fig. 506, to prevent the wood from absorbing the electrolyte.)

In the newer Eastern plants of the United States, the Walker tanks and their arrangement in blocks have met with general favor.

The details of the tank construction at the Raritan works are given in Figs. 511–515. The inner boards are only 1.75 in. thick, the outer planks the usual

3 in.; both boards and planks are connected by feather-joints. In a block two adjoining tanks are separated by an open space 1.75 in. wide with air-holes for ventilation; 3 tie-rods pass through such a space tying channel-iron buckstays, while in the two outer tanks of a block the rods are placed in openings drilled through the planks. The side walls do not extend to the top of a tank, but

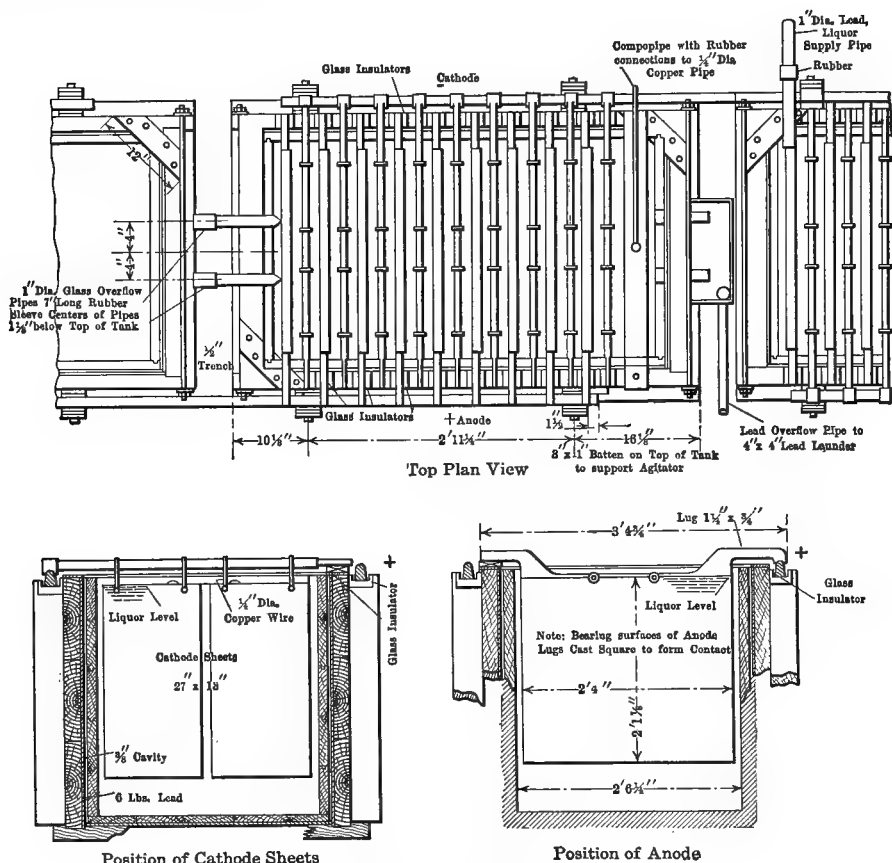


FIGS. 511-515.—Walker system of depositing vats.

are morticed in a cap, 9.25 in. high by 5.25 in. wide, which carries a maple board,  $7\frac{7}{8}$  by  $1\frac{1}{2}$  in., supporting a triangular bar,  $1\frac{1}{8}$  in. at base; the strong cap carries the large weight of the electrodes. The tanks rest on longitudinal sills, 8 by 8 in., standing upon isolating glass plates, 14 by 14 by 1 in., carried on 12- by 12-in. brick posts laid in cement. A tank bottom is usually lined with  $\frac{1}{2}$ -in. boards,

placed lengthwise, to protect the lead-lining from falling pieces of anode. At each end of the tank is a cross-board, held in place by brackets, which prevents the longitudinal boards from being floated.

The tanks of the Lithgow plant, N. S. W.,<sup>1</sup> given in Figs. 493, 516-518, are 4 ft. 2.75 in. by 2 ft. 6.25 in. and 2 ft. 9.5 in. deep; they are arranged in single rows of three tiers, each tier forming a cascade of eight tanks with 5 in. between adjoining tanks.



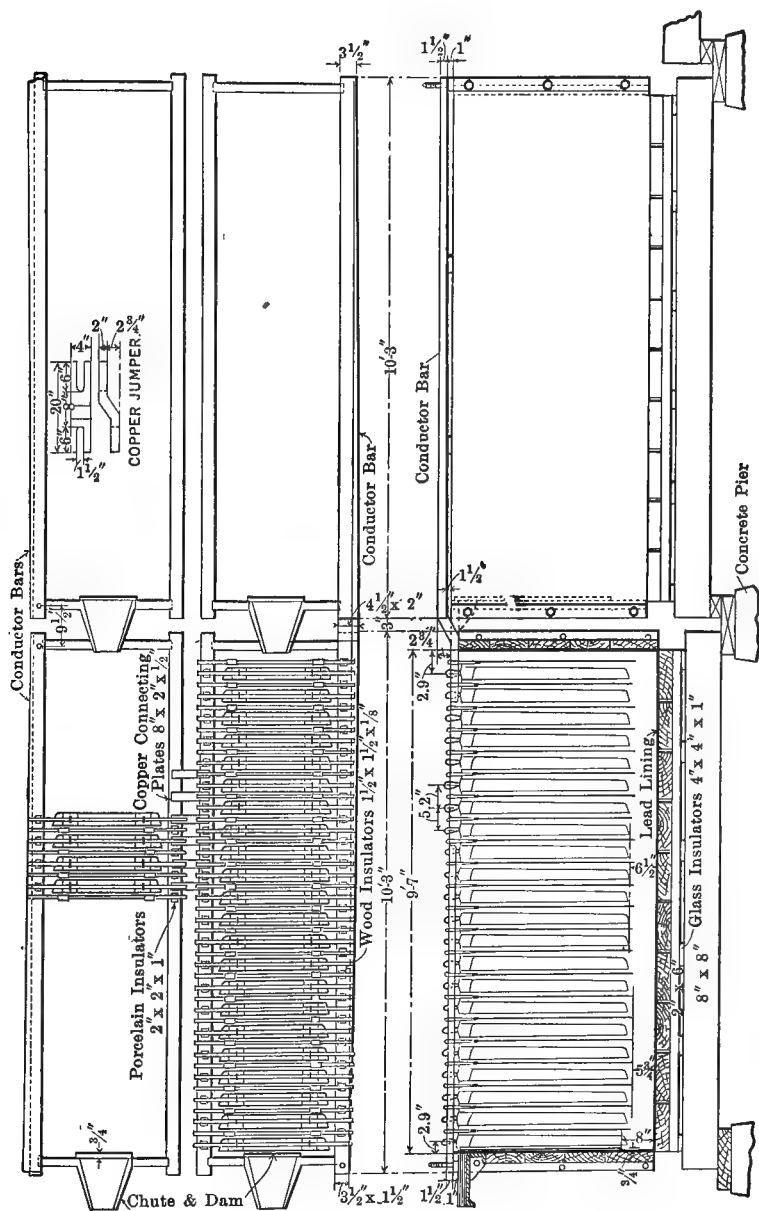
FIGS. 516-518.—Depositing vat of Lithgow, N. S. W.

Some interesting features of construction are to be noted. The tank is made of Oregon pine; there are an outer and an inner box, 3 and 2.25 in. thick, between which is placed the 6-lb. lead lining; the planks have been soaked for 10 min. in paraffine wax held at 60° C. The tanks rest on wooden longitudinal bearers, 5 by 3 in., carried by glass insulators which are supported by wooden blocks, 4 by 4 by 3 in., standing upon brick piers, 9 by 9 in.

The length of a tank depends upon the number of electrodes it is to hold.

<sup>1</sup> Blakemore, *Tr. Aust. Inst. Min. Eng.*, 1912, xv, 36; *Eng. Min. J.*, 1910, xc, 717, 769.

A common figure is perhaps 10 ft. with 20-22 anodes; at Chrome<sup>1</sup> there are at present 26 anodes in a tank. The width and depth vary with the size of the



FIGS. 519-520.—Depositing vats of Great Falls.

electrode. Ordinary dimensions are 2 ft. 8 in. and 3 ft. 9 in.; in recent years<sup>2</sup>

<sup>1</sup> Walker, *Min. Ind.*, 1910, XIX, 218.

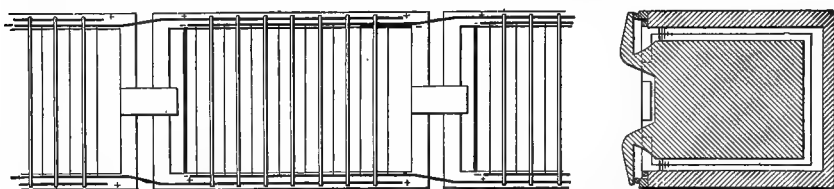
<sup>2</sup> Walker, *Eng. Min. J.*, 1911, XCI, 41.

anodes have been increased from 3 ft. wide by 2 ft. deep to 3 by 3 ft., which increases the necessary depth of tank by 12 in.

In all modern plants the tanks are placed on piers so as to leave head-room of about 9 ft. beneath for ventilation, discovery of leaks, etc.

The basement floor is made acid-proof by being built of chemical brick with joints filled with pitch; it slopes toward troughs ending in a sump.

A common electric connection of the depositing vats is shown diagrammatically in Figs. 488-489. It is typical for tanks arranged in single rows.



FIGS. 521-522.—Thofern electric connection.

The advantage is ready accessibility of contacts; the disadvantage, requirement of much floor space. Great Falls, Figs. 519-520, and Lithgow, Figs. 493, 516-518, may serve as examples.

The Thofern,<sup>1</sup> also intended for single rows of vats, is shown in Figs. 521-522. Two busbars are placed on the tops of the sides of a vat. An anode is suspended from two positive cross-bars and a cathode from two corresponding negative bars. No isolating blocks are required; the corrosion of the anode is said to

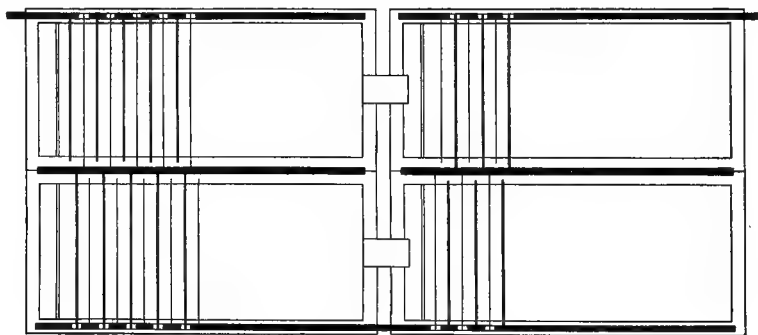


FIG. 523.—Arrangement of vats in pairs.

be more even, and the deposition upon the cathode more uniform. Whatever truth may lie in these claims, the facts are that an excessive amount of copper is tied up, and that twice as many contacts have to be kept bright as is necessary in the single-busbar arrangement. This method is the one favored in eastern refineries, as it gives a good contact, and locks up the least copper. The bars have to be well isolated from the vats; their supports are therefore made non-

<sup>1</sup> Hering, *Berg. Hüttenm. Z.*, 1893, LI, 54.



conductive by soaking wood in paraffine or similar substance, or by using glass. The cross-sectional area of a bar depends upon the amount of current that is to pass through it. With rectangular bars 1 sq. in. for 300 amp. used to be the standard; this was raised to 550 amp., but even with 1000 amp. they remain sufficiently cool; with triangular bars 400 amp. at the contact gives no trouble.

The cross-bars from which the electrodes are suspended are usually round bars of copper, 1 in. in diameter, flattened at the ends. Formerly they were made of soft steel copper-plated.

**259. Corrosion of Anode.**—According to their places in the electrochemical series, the metals electropositive to copper ought to go into solution before the copper, but with an anode of 98 per cent. Cu and over, there can be only a tendency in this direction. On the surface the more positive metal will be dissolved first, but the copper will follow closely. As the positive impurities as well as the  $\text{Cu}_2\text{O}$  are not evenly distributed, and parts of an anode will have cooled more quickly than others and become harder, the anode will not be evenly corroded; corrosion-pittings or hollows form; the free acid also acts chemically, especially at the contact of copper, electrolyte, and air. The result is that the anode becomes honey-combed, and even spongy if it was impure. Particles of copper fall off and collect in the anode mud. The purer the anode, the more even the corrosion. Usually the anode is removed in from 2 to 3 or 4 weeks, *i.e.*, before parts have become so thin that there is danger of a piece falling and thereby injuring the bottom lining of the vat or causing a short circuit, or both. In most cases the bottom of a vat is protected by boards (page 507). The weight of the corroded anode which goes back to the anode furnace amounts to about 10 per cent. of the original anode. Such anode scrap is placed in a hot-water tank and scrubbed with long-handle brushes to remove adhering anode mud. The necks are then cut off with shears to allow more compact charging in the reverberatory furnace.

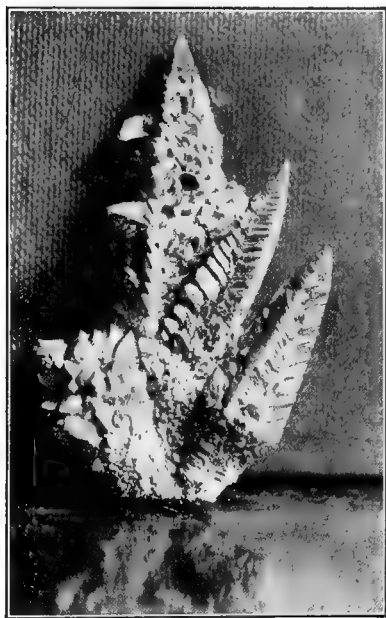


FIG. 524.—Electro-deposition crystals of copper.

**260. Deposition on Cathode.**—The purity of the cathode copper depends upon the purity of the anode, the slowness of deposition, the constancy of current, the composition, clarity, temperature, and circulation of the electrolyte, and lastly upon the prevention of anode matter coming mechanically in contact with the cathode. With a low current density the surface is crystalline,<sup>1</sup> solid, free from pin-holes, blisters, streaks,

<sup>1</sup> Huntington, *Eng. Min. J.*, 1905, LXXX, 1109.

etc. With the usual high current density, the deposit, smooth at first, soon becomes rough, shows knobs, especially near the edges, unless an addition of 0.01 per cent. of glue is made, which keeps the deposit smooth until the copper-content of the electrolyte falls below 2.5 per cent. This is accomplished, however, at the expense of voltage, which grows, probably on account of an increased transfer-resistance. The increase in voltage may reach 20 and even 30 per cent. with the usual extremely small amounts of glue charged.

In working with an insoluble anode, *i.e.*, with a potential of 2-2.5 volt, in purifying fouled electrolyte, there are formed at the edges of the cathode large crystals<sup>1</sup> as shown in Fig. 524.

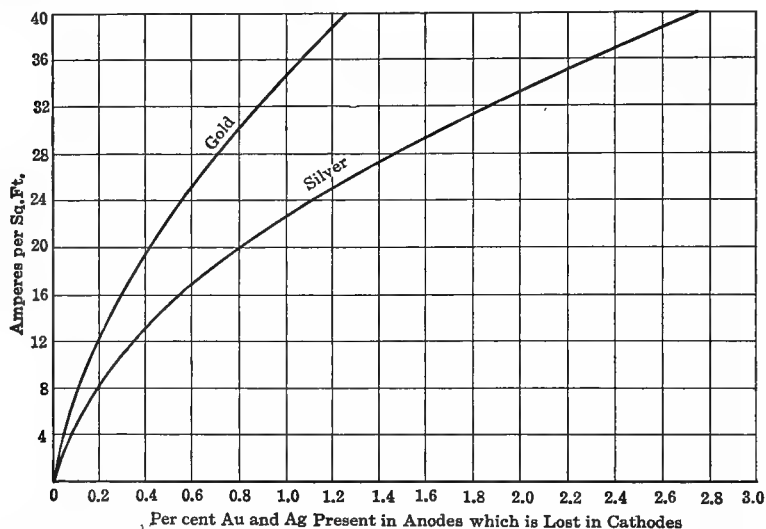


FIG. 525.—Relation between current-density and precious-metal losses (Addicks):

The deposition of copper in the form of tube, sheet, or wire is carried out on a large scale in Europe.<sup>2</sup> A discussion of details lies outside of the scope of this treatise.

The impurities in the cathode copper are either electrodeposited or mechanically occluded.<sup>3</sup> Under normal conditions no impurities are electrodeposited. Electrolyte enclosed between coarse crystals of copper does not play an important rôle, but if fouled by 1 per cent. As, it assists in the reduction of the electric conductivity. Cathode copper rarely contains <0.001 per cent. As. Mechanical contamination from floating slime, easily noticed by the Ag-content

<sup>1</sup> Addicks, *Electrochem. Met. Ind.*, 1905, III, 267.

<sup>2</sup> Cowper-Coles, *Electrochemist and Metallurgist*, 1904, III, 411; *Engineering Rev.*, 1905, XIII, 392; *Electrochem. Met. Ind.*, 1908, VI, 412.

Elmore, *Eng. Min. J.*, 1886, XLII, 315; 1888, XLVI, 124; 1890, L, 243; 1891, LI, 355, 463, 465, 713; LI, 238; 1892, LIII, 248; 1900, LXIX, 522; 1904, LXXVII, 197; 1905, LXXX, 35; *Electrochemist and Metallurgist*, 1903, III, 150.

<sup>3</sup> Emrich, *Tr. A. I. M. E.*, 1912, XLIII, 453.

of the cathode, is the most common source of impurity, as any local disturbance at the cathode may cause some slime to become suspended in the electrolyte, and to be floated to the cathode by electrostatic action.

In general, the Ag-content of the cathode is proportional to the anode. The gold-loss is about half the silver-loss. The relation between precious metal and current density is shown in Fig. 525 (Addicks).

The frequency with which cathodes are removed has already been referred to (page 505). The more frequent this is, the less the danger of short-circuiting, and the higher the efficiency of deposition. When the cathodes of a tank have been raised together, they are allowed to drain, are transferred to a water-tank to be dipped, and removed to a transfer car to be hauled to the refining furnace. The tarnished cross-bars are placed in bunches in a pair of suspended hooks, and washed in hot water by raising and lowering with a compressed-air cylinder. The round places for the loops are polished on an emery wheel, and the flat ends on an emery board.

**261. Anode Mud.**—The insoluble residue formed in refining is a black, slimy mass which amounts to 1 to 3 per cent. of the weight of the anode after coarse particles have been removed by passing through a 40-mesh screen. As practically all the 40-mesh material will pass through a 200-mesh screen, there is no necessity of using a screen finer than 40-mesh to separate metallics. The composition of the mud varies considerably with the character of the anode. Analyses are given in Table 122. Half of the copper of the mud is water-soluble, being present as finely divided  $\text{CuSO}_4 + \text{aq}$ . Slime from Montana is likely to run high in Te, that from Arizona in Se.

When anode mud has collected in sufficient quantity in the tanks of a cascade to be removed, these are cut out of service. The anodes as well as the cathodes of the lowest tank are removed with the overhead electric crane. The electrolyte is allowed to clarify for about 1 hr., and then drawn off either by siphons or through an opening in the side of the vat. The plug in the bottom is now drawn out and the slime sluiced out through a communicating trough into a stationary tank or movable slime-buggies. The plug is replaced, the electrolyte from the next higher tank is drawn off into the one just cleaned, whereupon new electrodes are put in place. The total operation lasts from 5 to 8 hr. according to the number of tanks.

The slime is screened through a coarse copper sieve (8-mesh) to remove particles of anode copper, and then through a 40-mesh screen; a centrifugal machine with bronze screen does the work quickly and effectively. In large works where much mud has to be handled, the stationary tank for receiving the mud from the mud-troughs may be a copper or bronze revolving drum which screens out the

<sup>1</sup> Addicks, *Min. Ind.*, 1900, IX, 271, 274.

Whitehead, *op. cit.*, 1901, X, 229.

Kroupa, *Oest. Zt. Berg. Hüttenw.*, 1903, LI, 173.

Betts, *Electrochem. Met. Ind.*, 1905, III, 141.

Kern, *Met. Chem. Eng.*, 1911, IX, 417.

TABLE 122.—ANALYSIS OF ANODE MUD

Great Falls, Montana.			Raritan, No. 2, Perth Amboy, N. J.		New Jersey		Baltimore		General U. S.		Kosaka	Great Cobar	General Range
Cu.....	12.90	14.80	43.3400	12.86	12.26	.....	11.0100	13.820	25	20	6.281	46.8	15-55
Ag.....	53.29	57.00	17.1870	26.58	53.68	37.83	53.8940	55.150	40	40	26.3708	15.5	5-50
Au.....	.....	.....	0.1200	0.36	0.28	2.24	0.2959	0.198	2	1	0.2602	1.5-4.0	0.02-0.70
Pt.....	.....	.....	6.000166	.....	.....	.....	.....	.....	.....	tr.	.....	.....	.....
Pb.....	tr.	5.26	0.7600	10.94	3.58	5.20	0.9100	2.070	18 (incl. SiO <sub>2</sub> , SO <sub>3</sub> , etc.)	2	12.965	.....	0.5-6.0
Sb.....	3.30	2.00	3.4600	16.21	6.76	8.00	6.2500	2.440	10	4	.....	.....	2-8
As.....	1.15	2.60	3.0300	7.13	5.42	5.30	2.1070	1.090	.....	4	.....	.....	1.5-6
Bi.....	1.55	5.70	0.1100	1.62	0.45	.....	3.9300	0.340	.....	2	.....	0.7	0.2-8
Ni.....	.....	.....	0.0800	0.90	0.30	0.75	1.00	.....	.....	3	.....	.....	.....
Co.....	.....	.....	0.0060	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Fe.....	.....	.....	0.3640	0.17	0.14	.....	.....	0.800	.....	.....	.....	.....	0.5-1.5
Zn.....	.....	.....	0.0900	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Se.....	2.0	.....	1.2000	3.82	2.30	2.40	0.3940	0.718	5	4	.....	0.65	0.1-2.5
Te.....	1.0	.....	2.1000	4.10	3.56	1.00	1.1740	0.892	.....	3	.....	.....	0.1-3.5
Si.....	.....	.....	0.1770	0.93 SiO <sub>2</sub>	0.93 SiO <sub>2</sub>	.....	.....	.....	.....	.....	.....	.....	.....
SO <sub>3</sub> .....	11.96	.....	13.2100 S	1.73 S	1.15 S	.....	5.2680	10.680	.....	4 S	.....	2.2 S	0.5-12
Cl.....	.....	.....	0.0260	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
H <sub>2</sub> O (250° C.).....	.....	.....	.....	.....	.....	.....	2.3650	2.664	.....	.....	.....	.....	.....
C.....	.....	.....	0.0500	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Ref.....	I	I	2	3	4	4	7	5	6	7	8	9	10

<sup>1</sup> Betts, *Electrochem. Met. Ind.*, 1905, III, 142. <sup>2</sup> Burns, *Tr. A. I. M. E.*, 1913, XLVI. <sup>3</sup> Aldrich, Private Communication, 1912. <sup>4</sup> Private Communication, 1912. <sup>5</sup> Keller, *Min. Ind.*, 1897, VI, 238. <sup>6</sup> Addicks, *J. Franklin Inst.*, 1905, CLX, 424. <sup>7</sup> Addicks, Private Communication, 1912. <sup>8</sup> Private Communication. <sup>9</sup> Kern, *Met. Chem. Eng.*, 1911, IX, 417. <sup>10</sup> Clark, *Met. Chem. Eng.*, 1912, X, 121.

particles of anode copper; the screened mud will then be raised to a storage tank by a centrifugal pump, after having been stirred up occasionally with an oar-like rod to prevent its packing down.

**262. Treatment of Anode Mud.**—Of the various methods suggested for treatment<sup>1</sup> four only are at present in use: direct fusion, lead-soaking, solution in  $\text{H}_2\text{SO}_4$  in the presence of air and  $\text{NaNO}_3$ , roasting followed by solution in  $\text{H}_2\text{SO}_4$ .

(1) **DIRECT FUSION.**—This is carried on in a reverberatory furnace with movable hearth fired with two oil-burners. The oval hearth is 8 ft. long, 6 ft. wide and 10 in. deep; consists of a cast-iron bed-plate and a  $\frac{3}{8}$ -in. wrought-iron ring; and is rammed with a mixture of 2800 lb. dolomite, 1800 lb. cement, and 1150 lb. fire-clay to a thickness at the sides, front, and back of 12 in. and at the bottom of 4 in. The side lining encloses a 2-in. water-cooled pipe. The stored mud is stirred up, drawn into a pressure-tank, and filtered in a press 3 ft. in diameter with 14 plates. The filtrate passes through 8 settling tanks placed in series, which collect any mud that may have passed through the cloth, and flows into the storage tank of the tank room. The 3-in. cakes are discharged into a car, to which is added soda-ash and siliceous ore rich in precious metal. The mixture is fed into the furnace at intervals at the sides near the burners; the slag flows off at the front. A furnace treats in 24 hr. about 5 tons of mud (Table 122, New Jersey), burns 500–600 gal. oil, makes 2.5 tons slag (Table 124, New Jersey), 0.5 ton flue-dust (Table 125), and doré silver, 0.820–0.860 fine. The slag goes back to be smelted, the silver is further purified in a lead cupelling furnace, and the flue-dust is passed through a suspended sheet-iron oval flue (4 by 3 ft. and 200 ft. long) with discharge doors in which the temperature is reduced to  $125^\circ\text{C}$ . before the gases enter a wet scrubber which collects most of the remaining dust and fume. The collected dust is treated in the dry way, by mixing with litharge and smelting in a reverberatory furnace, or in the wet way (see below).

Direct fusion is applicable only in a refinery that is connected with a lead plant to take care of the intermediary products.

(2) **LEAD-SOAKING.**—The filter-pressed cakes of slime are partly dried and charged in paper bags, from 10 to 15 lb. at a time, onto the lead bath of a cupelling furnace, when the copper and other impurities are readily oxidized and scorified. As coppery litharge has a strongly corroding effect, the cupel should be water-jacketed and in addition lined with magnesite brick.

(3) **SOLUTION IN  $\text{H}_2\text{SO}_4$  WITH AIR AND  $\text{NaNO}_3$ .**—The steps taken are: solution of copper with disposal of blue vitriol; filtering, washing, and drying of residue; oxidizing fusion in a reverberatory furnace with blast and niter, and withdrawal of slags until the silver or doré silver is fine;<sup>2</sup> and casting into marketable form or into plates suited for parting. A few examples may serve to show details:

**EXAMPLE I.**—The slime is screened through a 1-in. and then an 8-mesh

<sup>1</sup> Ulke, *Min. Ind.*, 1893, II, 278.

<sup>2</sup> The alloy-series  $\text{Ag-Cu}_2\text{O}$  has been studied by Mathewson and Stokesbury, *Internat. Zt. Metallographie*, 1914, V, 193.

sieve placed on a circular stationary vat to remove coarse anode copper; the remaining metallics are screened out by passing the mud through a centrifugal machine with a 40-mesh sieve. The slimy mud assaying Ag 50 and Au 0.5 per cent. is transferred into an oblong wooden lead-lined vat on the bottom of which lies a zig-zag lead-pipe perforated on the upper side. Dilute  $\text{H}_2\text{SO}_4$  (1:4) is drawn into the vat and heated air injected through the pipe. This stirs the mud, heats the solution and furnishes the necessary O. Solution and mud are discharged into a settling tank; the clarified liquor is siphoned off; the mud is washed three or four times by decantation, filter-pressed, and washed until sweet. The cakes from the press are partly dried and melted in a water-jacketed cupelling furnace. A small amount of slag, assaying Pb 20 per cent. and Sb < 10 per cent., is formed and drawn off; then niter is charged, which forms a slag with as much as 20 per cent. Te.<sup>1</sup> This is drawn off, and more niter is added until the silver is fine and ready for casting.

EXAMPLE II.<sup>2</sup>—The slime is screened through a copper plate with 1-in. holes and a lead plate with slots equivalent to a 40-mesh wire screen, into a tank, whence it is transferred by a centrifugal pump to three storage tanks 4 by 4 by 10 ft. in the silver-refinery,<sup>3</sup> where the slime, assaying 50 per cent. Ag and 30 per cent. Cu, settles, while the overflow goes back to the tankhouse. The mud is transferred into seven circular hard-lead agitators, 6 ft. in diameter and 5 ft. deep, with vertical steel lead-covered shafts and hard-lead paddles making 15 r.p.m. A charge consists of 6,000 lb. wet mud (= 3,000 lb. dry), 2,600 lb.  $\text{H}_2\text{SO}_4$  66° Bé., 250 lb. niter, and water; it is heated with live steam and air is pumped in to assist the oxidation. Boiling, which usually lasts 8 hr., is continued until silver goes into solution, when the necessary correction is made by adding fresh mud. The solution (Cu 4-5, As 0.4, free  $\text{H}_2\text{SO}_4$  15 per cent.) and decopperized mud are drawn into a lead-lined cast-iron acid egg and forced through a Bushnell filter press, 27 by 27 in., with 40 plates and frames of hard lead. Table 123 gives analyses of raw and of treated mud.

TABLE 123.—ANALYSES OF RAW AND OF TREATED MUD

Mud	Se	Te	As	Sb	Bi	Pb	Cu	Fe	Ni	S	SiO <sub>2</sub>	Ag	Au
I Raw <sup>a</sup> ....	3.82	4.10	7.13	16.21	1.62	10.94	12.86	0.17	0.09	1.73	0.53	26.58	0.36
Treated..	4.20	4.10	7.73	19.81	1.53	13.18	2.81	0.09	0.09	1.92	0.40	30.72	0.42
II Raw <sup>a</sup> ....	2.30	3.56	5.42	6.76	0.45	3.58	12.26	0.14	0.03	1.15	0.93	53.68	0.28
Treated..	2.54	4.28	3.61	7.21	0.54	4.10	3.02	0.13	0.03	1.29	1.02	63.36	0.31

The mud, which usually contains < 1 per cent. Cu, is washed, discharged, and smelted with the addition of niter in an air-blown, oil-fired (1½-in. Rockwell burner) reverberatory furnace<sup>4</sup> with a hearth 8 ft. 3 in. by 5 ft. 7 in., lined with 9 in. magnesite, sides and bottom. A charge of 17,500 lb. moist (20 per cent.  $\text{H}_2\text{O}$ ) slime is smelted in 48-72 hr. with 2,000 lb. niter and 200-250 lb. soda-

<sup>1</sup> Whitehead, *J. Am. Chem. Soc.*, 1895, XVII, 849.

<sup>2</sup> Raritan: Addicks, *Min. Ind.*, 1900, IX, 261; Private Notes, 1907 and 1913.

<sup>3</sup> Plan given in *Electrochem. Met. Ind.*, 1908, VI, 277.

<sup>a</sup> Have been given in Table 122.

<sup>4</sup> Drawing, *Electrochem. Met. Ind.*, 1908, VI, 277.

ash, with a consumption of 200–250 gal. oil; it furnishes about 5,000 lb. doré silver of a fineness of Ag 0.984, Au, 0.15, Cu 0.1, which is cast into anodes 11.5 by 7.5 by 0.5 in. to be parted electrolytically by the Balbach-Thum process.

(4) ROASTING AND SOLUTION IN  $H_2SO_4$ .—The slime freed from metallics by a 40-mesh sieve is filter-pressed; the disintegrated cakes are charged into a muffle furnace and heated to oxidation, which begins below a visible red. When once started, the smoldering roast progresses of its own accord.<sup>1</sup> The roasted slime is pulverized, treated with hot dilute  $H_2SO_4$  for 8–10 hr. in a tank, say 8 ft. in diameter and 8 ft. high, having a mechanical stirrer. A total of 13,000 lb. leached slime is melted in an oil-fired reverberatory furnace with hearth 5 by 12 ft. and 15 in. deep, lined with magnesite brick; it takes 30 hr. to melt the material, charged at short intervals. Niter flux from a preceding charge is added to assist in liquefying the slag, which is skimmed and goes to the anode furnace (3000 oz. per ton) or the ore-furnace (1000 oz. per ton). There forms on the metal bath a dark cherry-colored selenide of copper and silver (Cu 33, Ag 33, Se 33 per cent.) which is oxidized by rabbling and by forcing air through the bath by means of an iron pipe.<sup>2</sup>

The flue-dust collected, rich in precious metal, contains from 30 to 50 per cent. Se and Te, both of which are recovered. To the bath is added soda-ash to purify the metal. The slag formed is skimmed, and fresh flux is added until the slag ceases to become dark, whereupon soda-ash and niter are charged to fine the silver. After the first 13,000 lb. of decopperized anode mud have been thus treated and a bath of more or less pure silver has been obtained, more mud is charged and refined until the furnace has received its complement of 22,000 lb. mud, the total treatment of which takes four and one-half days and furnishes 7000 lb. doré silver.

Table 124 gives analyses of reverberatory slags obtained in the fire-refining of anode mud, and Table 125 analyses of flue-dust and scrubber-sludge.

TABLE 124.—REVERBERATORY-SLAGS FROM ANODE MUD

No.	As	Sb	Se	Te	Cu	Pb	Bi	Ag	Au
I	3.8	7.3	2.3	1.2	8.4	10.4	.....	11.604	0.0003
II	.....	.....	.....	.....	15.4	14.6	.....	8.747	0.0014
III	.....	.....	.....	.....	9.6	12.2	.....	3.220	0.0031
IV	.....	.....	.....	.....	7.3	7.0	.....	5.396	0.0048
V	3.05	14.3	2.3	4.5	6.56	14.05	2.25	2.28	0.0063

TABLE 124.—REVERBERATORY-SLAGS FROM ANODE MUD—(Continued)

No.	SiO <sub>2</sub>	Insol	FeO	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Ni	S	Mn
I	14.2	34.0	2.5	.....	.....	.....	1.43	.....	.....
II	13.3	.....	.....	.....	.....	.....	.....	.....	.....
III	16.9	.....	.....	.....	.....	.....	.....	.....	.....
IV	15.0	.....	1.8	0.8–2.1	.....	.....	.....	.....	.....
V	14.4	.....	2.25	4.75	2.34	2.50	0.03	0.27	trace

<sup>1</sup> See also, p. 478.

<sup>2</sup> Behavior of Ag and O: Kohlmeier, *Chemiker Z.*, 1912, XVIII, 151, 211.

TABLE 125.—ANALYSES OF FLUE-DUST AND SCRUBBER SLUDGE FROM REFINING ANODE MUD

	As	Sb	Se	Te	Cu	Pb	Bi	Ag	Au	SiO <sub>2</sub>	FeO	CaO	Ni	S
Flue-dust.....	4.80	13.90	5.20	3.10	1.00	0.70	....	4.018	0.002	.....	.....	.....	.....	....
Flue-dust.....	9.00	25.30	3.00	1.60	....	....	....	....	....	....	....	....	....	....
Scrubber sludge....	12.18	39.01	4.50	3.00	0.61	0.34	2.88	1.98	0.013	0.35	8.10	0.40	trace	0.97

The gases and fumes from the reverberatory furnace treating anode mud are always passed through cooling flues and thence through scrubbers. At the refinery of the Raritan Copper Co. the gases leaving the scrubbers are further treated in a Cottrell electric condenser.<sup>1</sup> In its leading features it resembles the apparatus used at the Balaklala smelter, discussed in connection with Figs. 246-247; in detail it differs to meet the new conditions. Figs. 526-528 give a plan and horizontal section, a section and side-elevation, as well as a section and end-elevation of the condenser with its connections. It consists of a lead-lined plate-iron tank, 18 ft. long by 8 ft. 5½ in. wide and 6 ft. deep; the bottom is hopper-shaped to catch and deliver the sludge to a settling tank; the top is covered with planks provided with handles near the ends. The tank has two sets of 14 longitudinal parallel iron bars, about 3 ft. 6 in. long, resting on cross-pieces connected at the ends with the two branches of the positive pole. From each bar are suspended rod-shaped iron positive discharges about 5 ft. long. The number of positive poles, 26 used at the start, has been reduced to 18. Parallel with the longitudinal positive bars are suspended sheet-lead negative grounded poles; eight of these plates are held in the slots of two lead-covered rectangular rolled iron bars.

The motor and alternator are in separate buildings.

They are combined as a rotary converter, the direct-current end being wound to 220 volts, the alternating end to about 158 volts, single phase. The rotary converter is rated at 2 kw., and is mounted on a shaft. Connected to the rotary converter shaft is a micanite disc carrying two segments of copper. The brushes carrying the current to the rectifier have a rotary adjustment for properly regulating over the lag of the current. The transformer is oil-cooled, 7.5 kw. capacity, with 10 taps for transforming the current from 35,000 to 50,000 volts. The input direct current is about 10 amp., and, of course, 220 volts, while the rectified current is a few milliamperes at about 40,000 volts.

The condenser is designed to treat 10,000 cu. ft. gas per minute; at present about 6500 cu. ft. gas with 0.0258 g. solid matter per cubic foot pass through it; a clearance of about 90 per cent. of solids is effected. The condensed matter runs high in Ag and low in Au.

**263. Recovery of Tellurium and Selenium.**—It was shown on p. 516, that the niter slag obtained in refining anode mud in the reverberatory furnace contained as much as 20 per cent. Te.

There are two ways of recovering the Te although they are not much carried on because so far there is little industrial use for the metal.

One method consists in dissolving the slag in hot water, filtering and evaporating, if necessary, to the right degree of concentration, and then electrodepositing the metal, using lead electrodes.

<sup>1</sup> Hofman, "General Metallurgy," 1913, p. 858.



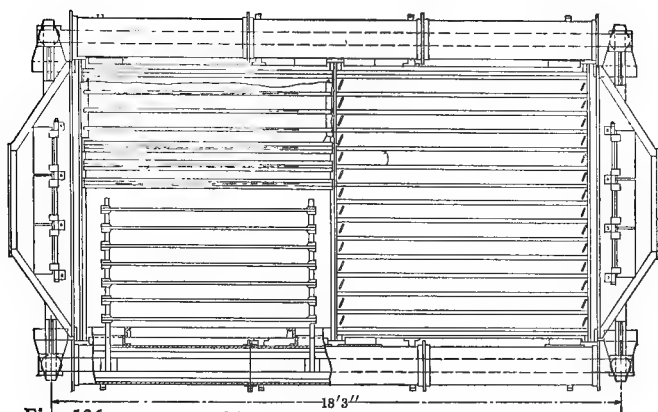


Fig. 526 Plan and Horizontal Section

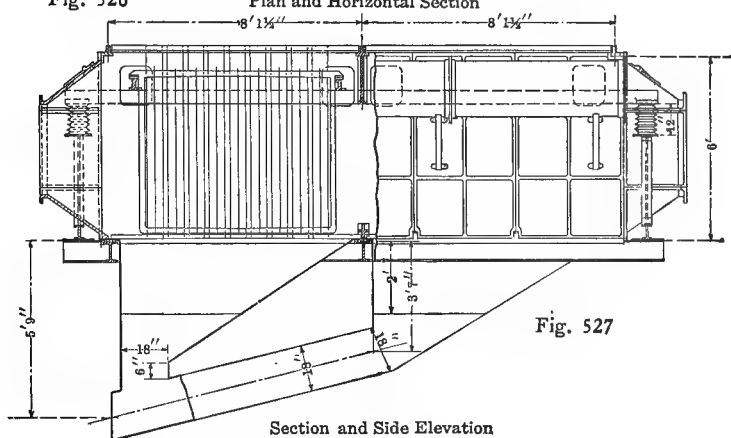


Fig. 527

Section and Side Elevation

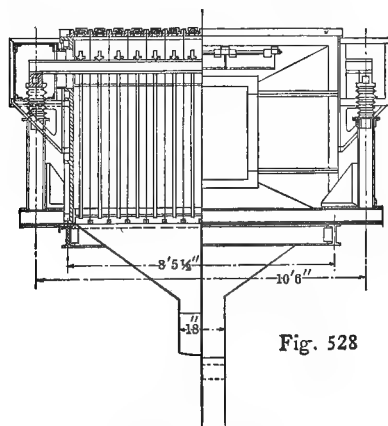


Fig. 528

Section and End Elevation

FIGS. 526-528.—Cottrell electric condensation of the Raritan Copper Co.

The other method is based upon the reaction which takes place when the filtered hot alkaline aqueous solution is just acidified with  $\text{H}_2\text{SO}_4$ , and causes  $\text{Na}_2\text{Te}_2\text{O}_3$  to fall out. From the filtrate, Se can be precipitated by means of  $\text{SO}_2$ -gas. Most Se on the market is produced from the grayish flue-dust collected in the cooling flues of the reverberatory furnace treating anode mud.

Scrubber liquors which contain Se must be concentrated to about  $20^\circ \text{Bé}$ . before they can be treated for Se; the present price of the metal does not warrant treating the liquors.

Flue-dust with 20–25 per cent. Se is treated in charges of 70 lb. in a 125-liter jar with 15 lb. commercial  $\text{HCl}$ , 10 lb.  $\text{KClO}_3$  or  $\text{NaNO}_3$ , and water, stirred, and allowed to settle. When clear, the supernatant liquor is siphoned off, the residue washed with  $\text{H}_2\text{O}$  by stirring, settling, and decanting or siphoning until the water-wash has a density  $5^\circ \text{Bé}$ . or less. To 4 vol. of Se-solution are added 2 vol. of commercial  $\text{HCl}$ , or enough to have 15 per cent. free  $\text{HCl}$ ; the whole is warmed and  $\text{SO}_2$ -gas, generated by burning S, passed through the vat, when at about  $80^\circ \text{C}$ . practically all the Se will be precipitated as a reddish powder. The temperature of the solution rises during the precipitation. The precipitate is settled, filtered through a wet filter, washed with cold water, and dried quickly in porcelain dishes on a hot steam table. The red precipitate shrinks to a bluish to brownish-black cake, and squeezes out some water charged with impurity. The dried Se is placed in a kettle, heated for about 4 hr. on a stove the top of which becomes barely red hot. In melting, a crust forms on the fluid metal; the latter is poured off into an enameled mold, the crust is brought to a higher temperature whereupon more fluid Se is eliquated; finally the crust itself is liquefied and cast into molds.

Details of the practice at the few plants producing Se vary considerably and are not available.

**264. Foul Solutions.**<sup>1</sup>—The electrolyte in time becomes overcharged with impurities such as As, Sb, Bi, Ni, Fe, which interfere with the quality of the cathode deposit, and with the blue vitriol which is recovered by crystallization. A fouled electrolyte from Great Falls<sup>2</sup> contained per liter, Cu 51.8, Fe 13.2, As 14.02, Sb 0.62,  $\text{H}_2\text{SO}_4$  48 g.; the low percentage of Sb is due to the addition of enough  $\text{HCl}$  to the head tank to maintain 0.04 g. Cl per liter in the solution.

There are two general methods for purifying the electrolyte; one is direct removal of impurities by precipitation, the other withdrawal of part of the foul electrolyte and its replacement by blue vitriol and the necessary free  $\text{H}_2\text{SO}_4$  while the foul solution is being treated.

The direct removal of impurities by precipitation has not been sufficiently successful in practice to become adopted. Thus, boiling with metastannic acid in order to precipitate As; filtering through oxidized granulated copper to throw down Sb and Bi; blowing air through the solution heated to  $35^\circ \text{C}$ . and over, to

<sup>1</sup> Ulke, *Min. Ind.*, 1897, VI, 239; *Zt. Electrochemie*, 1898, IV, 309; *Berg. Hüttenm. Z.*, 1898, LVII, 264.

Burns, *Tr. A. I. M. E.*, 1913, XLVI.

<sup>2</sup> Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 312.

oxidize  $\text{FeSO}_4$  and cause it to fall out as a basic ferric sulphate, accompanied perhaps by Sb- and Bi-salts, have all been tried and given up again.

The general practice is to withdraw continuously one or more per cent. of the electrolyte from the main stream, purify it, and allow fresh electrolyte or purified solution to flow into the head tank.

The following methods of purification may be considered as covering the ordinary modes of operating:

CRYSTALLIZATION, suited for an electrolyte practically free from Ni.

CRYSTALLIZATION FOLLOWED BY ELECTRODEPOSITION, suited for an electrolyte heavily charged with Ni.

ELECTRODEPOSITION, suited for an electrolyte lightly charged with Ni.

(a) THE CRYSTALLIZATION METHOD.—The free acid is neutralized, or rather reduced to below 1 per cent., by dissolving in it granulated copper in the presence of air, Vitriolization Process, § 243. The neutral or slightly acid liquor is concentrated in lead pans by steam coils to  $43^\circ$  Bé. and then crystallized, whereafter, in the absence of  $\text{NiSO}_4$ , from 85 to 90 per cent. of the blue vitriol can be recovered of a sufficient purity to permit re-solution and crystallization for a marketable product. Following is an analysis of impure crystals:<sup>1</sup> Cu 32.78, Fe 0.589, Ni 0.0496, Pb 0.0122, Bi 0.0640, Sb 0.2920, As 0.2470 per cent.

The copper remaining in the mother liquor is recovered in two ways. It is precipitated by Fe with the As and Sb that is present; the first precipitate is kept separate from the last, as this may contain as much as 60 per cent. As and form the raw material for the manufacture of arsenical compounds.

In the second method the liquor is concentrated to the point at which both sulphates of Cu and As crystallize together; the crystalline mass, separated from the mother liquor, is treated with just enough water to dissolve the copper sulphate; the residual arsenical salt is suited for the production of copper-arsenic salts.

Drawings of the Sulphate Building of the first electrolytic refining plant of Great Falls, Mont., have been published by Burns (*loc. cit.*).

As regards the separation of  $\text{CuSO}_4$  and  $\text{NiSO}_4$  by fractional crystallization, it is held<sup>2</sup> that if an acid solution at  $35^\circ$  C. contains an excess of  $\text{CuSO}_4$  over a presupposed cryohydrate of  $2\text{NiSO}_4 + x\text{H}_2\text{O}$ :  $1\text{CuSO}_4 + y\text{H}_2\text{O}$ ,  $\text{CuSO}_4 + x\text{H}_2\text{O}$  will separate, but that with an excess of  $\text{NiSO}_4$ , there will be formed crystals of  $\text{NiSO}_4 + 7\text{H}_2\text{O}$ . The ordinary  $\text{CuSO}_4 + 5\text{H}_2\text{O}$ <sup>3</sup> gives up 2 mol.  $\text{H}_2\text{O}$  at  $28^\circ$  C., and  $\text{NiSO}_4 + 7\text{H}_2\text{O}$  loses 2 mol.  $\text{H}_2\text{O}$  only, at  $40^\circ$  C.

(b) CRYSTALLIZATION FOLLOWED BY ELECTRODEPOSITION.—The electrolyte is concentrated to  $46$ – $47^\circ$  Bé. in wooden lead-lined tanks with steam coils carried by cast-lead frames. A tank 16 by 15 ft. and 4 ft. 10 in. deep with 350 ft. of 1.5 in. lead pipe will evaporate in 24 hr. 1000 cu. ft. liquor of 1.240 sp. gr. to 340 cu. ft. 1.460 sp. gr. The concentrated solution is run into a crystallizing tank

<sup>1</sup> Keller, *Min. Ind.*, 1898, VII, 238.

<sup>2</sup> Private Communication by C. S. Witherell, 1912.

<sup>3</sup> Hofman-Wanjukow, *Tr. A. I. M. E.*, 1912, XLIII, 523.

constructed to cause a rapid separation of crystals. Such a tank 12 by 6 ft. and 4 ft. deep with eight cross-timbers, 6 by 6 in., each carrying eight rows of vertical zigzag 1-in. water-cooled lead pipes will cause 82 per cent. of the copper to crystallize in 48 hr. in the form of small crystals which carry some  $\text{NiSO}_4 + \text{aq}$ . The mother liquor goes to the liberating tanks; water is run into the crystallizing tank, steam is turned on, the crystals are dissolved, mud is allowed to settle, and the liquor run to the tank house. The liberating tanks receiving the mother liquor are depositing tanks, with sheet-lead anodes and sheet-copper cathodes, in which all the copper and some of the arsenic are deposited in a sufficiently coherent condition to permit scraping off the deposit with a chisel-pointed bar, and are turned over to the smelting department. A liberating tank has the same dimensions as a depositing tank. There are usually provided 1.5 to 2 liberating tanks for every 100 depositing tanks. The electromotive force required ranges from 2 to 2.5 volts.

In order to hold back in the bath the choking fine particles of  $\text{H}_2\text{SO}_4$  which are carried off into the air with the O liberated at the anode, the electrolyte is covered with a layer of oil. In some instances accidents have occurred on account of the formation of  $\text{AsH}_3$ ; hence at several works these tanks are placed in an open shed.

The further treatment of the copper-free solution containing, *e. g.*, Ni 1+ per cent., As 1 per cent., free  $\text{H}_2\text{SO}_4$  15 per cent., varies somewhat.

The  $\text{As}_2\text{O}_5$ -salts are first reduced to the  $\text{As}_2\text{O}_3$ -stage with  $\text{SO}_2$ -gas by allowing the solution to run down one covered cascade in which the gas ascends, and then  $\text{As}_2\text{S}_3$  is precipitated by  $\text{H}_2\text{S}$  in a second cascade. The arsenic-free solution is concentrated in a series of lead pans (twelve, 6 by 4 ft. and 13 in. deep) followed by iron pans (four round-bottomed of the same dimensions), with the fire-place beyond the last iron pan. The fire-gases pass under the iron pans and then under the lead pans, while the liquor flows in the opposite direction leaving the last iron pan at a concentration of from 72–75 per cent. free  $\text{H}_2\text{SO}_4$  to be collected in an iron pan where, upon cooling,  $\text{NiSO}_4$  contaminated with 1–2 per cent.  $\text{FeSO}_4$  falls out. The nickel-free acid goes to the tank house. The  $\text{NiSO}_4$  and  $\text{FeSO}_4$  are dissolved in  $\text{H}_2\text{O}$ , the  $\text{FeSO}_4$  is oxidized with  $\text{CaClO}_4 + \text{CaCl}_2$  in the cold and precipitated with  $\text{CaCO}_3$ . The purified  $\text{NiSO}_4$  is evaporated to dryness in a pan, and calcined in a reverberatory furnace to drive off  $\text{H}_2\text{O}$  and  $\text{SO}_3$ . The  $\text{NiO}$  is mixed with charcoal and smelted in an oil-fired reverberatory furnace at the rate of 1.5 tons in 24 hr. and is either cast into ingots in upright split molds, or shotted after the C it had absorbed has been removed by additions of  $\text{NiO}$ .

Instead of concentrating the copper-free liquor in a single operation, two steps are taken, steam-concentration to 50° Bé, and direct-fire concentration in a V-shaped boiler-iron tank to 72 per cent.  $\text{H}_2\text{SO}_4$ . The resulting  $\text{NiSO}_4$  may be freed from part of its  $\text{H}_2\text{SO}_4$  by placing on a quartz filter, transferring to an inclined lead-covered drainage-floor, placing on a perforated lead plate provided with suction, and adding a small amount of wash-water. The crystals will contain Ni 31 per cent. and free  $\text{H}_2\text{SO}_4$  8 per cent. The  $\text{NiSO}_4$ -crystals

from the solution with 72 per cent.  $\text{H}_2\text{SO}_4$  may be freed from most of their  $\text{H}_2\text{SO}_4$  by washing with a little water in a centrifugal machine. Copper- and nickel-free concentrated acid may be freed from As by boiling with charcoal, which reduces  $\text{As}_2\text{O}_5$  to  $\text{As}_2\text{O}_3$ , and precipitating by diluting to  $40^\circ \text{Bé.}$ ; the  $\text{As}_2\text{O}_3$  settles readily and with it the coloring  $\text{C}_2\text{H}_4$  formed in the treatment with charcoal.

At Great Falls, Mont.,<sup>1</sup> the electrolyte is purified in the following manner. From the 320 tanks (9 ft. 7 in. by 2 ft. 4 in. and 3 ft. 9 in. deep) there are withdrawn daily 25,000 liters electrolyte to be purified. The solution, concentrated to  $48^\circ \text{Bé.}$ , is drawn into crystallizing tanks, and remains there 4 days, during which 82 per cent. of the Cu crystallizes out. The resulting mother liquor, containing  $\text{H}_2\text{SO}_4$  475, Cu 17.4, As 20.2, Sb 1.1, Fe 15.2 g. per liter, is electrolyzed in four purifying tanks, of the above dimensions, containing lead anodes and copper cathodes. With a circulation of 7 liters or nearly 2 gal. per minute (depositing tanks have one of 6 gal. = 22.5 liters) there are removed 99 per cent. of the Cu, 78 of the As, 91.1 of the Sb with an ampere-efficiency of 50 per cent. The more or less slimy cathode deposit contains  $\text{H}_2\text{O}$  9.66, Cu 46.30,  $\text{SiO}_2$  0.38, FeO 1.66,  $\text{Al}_2\text{O}_3$  0.4, CaO 1.08, S 5.02, As 21.48, Sb 2.28, Ni 0.35, Zn 0.32 per cent., Ag 3.61 and Au 0.03 oz. per ton.

The changes taking place in the electrolyte of the four tanks placed in series, with a circulation of 4 liters per minute; are shown in Table 126. Correcting

TABLE 126.—REMOVAL OF CU, AS, AND SB FROM ELECTROLYTE IN INSOLUBLE-ANODE TANKS  
(Circulation, 4 liters per min.—9000 amp; 31.8 amp. per sq. ft.)

Tank	Grams per liter					Volts per tank	Temperature, deg. C.
	$\text{H}_2\text{SO}_4$	Cu	Fe	As	Sb		
Inlet tank No. 1.....	144	37.060	6.242	3.200	0.463	.....	17
Outlet tank No. 1.....	184	7.376	6.813	2.240	0.260	2.22	42
Outlet tank No. 2.....	194	0.504	7.364	0.400	0.061	2.25	57
Outlet tank No. 3.....	208	0.088	7.701	0.056	0.038	2.25	64
Outlet tank No. 4.....	216	0.048	7.915	0.028	0.028	2.25	65

TABLE 127.—ANALYSES OF TABLE 126 CORRECTED TO BASIS OF CONSTANT VOLUME OF ELECTROLYTE

Tank	Grams per liter					Percentage elimination of original amounts			Ampere-efficiency, per cent.
	$\text{H}_2\text{SO}_4$	Cu	Fe	As	Sb	Cu	As	Sb	
Inlet tank No. 1.....	144	37.060	6.242	3.200	0.4630	.....	.....	.....	.....
Outlet tank No. 1.....	169	6.760	6.242	2.050	0.2380	81.8	35.9	48.7	71.70
Outlet tank No. 2.....	165	0.427	6.242	0.339	0.0517	17.1	53.5	40.2	19.50
Outlet tank No. 3.....	169	0.071	6.242	0.045	0.0308	0.9	9.2	4.7	1.68
Outlet tank No. 4.....	170	0.038	6.242	0.022	0.0220	0.1	0.7	1.7	0.15
Totals and averages.....	.....	.....	.....	.....	.....	99.9	99.3	95.3	23.26

<sup>1</sup> Burns, *loc. cit.*

the analyses for a basis of unchanged volume of solution (in which  $\text{Fe} = 6.242$  g. per liter) gives the data in Table 127. This shows that while the percentage-deposition of Cu, As, and Sb with a circulation of 4 liters per minute is much higher than with one of 7 liters, the ampere-efficiency has fallen from 50 to 23.26 per cent.

The electrolyte freed from most of its Cu, As, and Sb, still retains Fe, Ni, Bi and Zn. In order to remove these, the liquor is transferred to a lead-lined tank (13 ft. in diameter and 4.5 ft. deep, lined with 12-lb. chemical sheet lead, provided with 600 ft. of 1-in. 8-lb. lead pipe), concentrated to  $55^\circ \text{Bé.}$ , run into an open tank 10 by 4 ft. and 3 ft. deep, allowed to stand for 4 days; during which Fe, Ni, Bi, and Zn will crystallize as sulphates, leaving behind a mother liquor with  $\text{H}_2\text{SO}_4$  1100, As 1, Sb 0.2, Fe 1, Ni 5.3, Zn 1.5 g. per liter.

Originally the electrolyte cut out from the main stream was run direct into the insoluble-anode tanks. The deposit was in the form of a black slime which in part adhered to the cathode and in part collected on the bottom of the tank. Its composition was  $\text{H}_2\text{O}$  10.0 per cent., Cu 55.1,  $\text{SiO}_2$  1.1,  $\text{FeO}$  0.4,  $\text{Al}_2\text{O}_3$  0.4,  $\text{CaO}$  0.3, S 4.1, As 10.3, Sb 2.5, Ni 0.35, Zn 0.32 per cent., Ag 3.4 and Au 0.02 oz. per ton. The method was abandoned because the ampere-efficiency was much lower, and the amount of slime produced much higher than when 82 per cent. of the Cu had been first removed by crystallization.

(c) ELECTRODEPOSITION.—In the liberating tanks as much puré copper as is feasible is deposited, leaving only a small amount of impure copper containing most of the arsenic and antimony. This fractional deposition is accomplished by retarding the flow of solution in the liberating tanks in which the arsenic is to come down. The separated arsenical copper, and the impurities, in part adhere to the cathode, and the remainder falls to the bottom and forms a dark mud. The acid freed from As and Sb goes to the tank-house. If it should be too rich in Fe, it is concentrated to about one-third its volume and cooled, whereby most of the Fe will crystallize.

**265. Costs.**—The cost of a multiple electrolytic plant is great on account of the large amount of copper and blue vitriol locked up. Thus at Great Falls, Mont.,<sup>1</sup> with 300 tanks, 9 ft. 7 in. by 2 ft. 4 in. and 3 ft. 9 in. deep, each holding an electrolyte with 3.280 per cent. Cu, 22 anodes weighing 500 lb. and 22 cathodes weighing 2.5 lb., and with a daily production of 174,000 lb. copper, employing a current density of 34 amp. per square foot and 2-day cathodes, there are locked up in anodes 2,300,000 lb. Cu, 44,000 oz. Ag and 316 oz. Au; in slime 27,300 lb. Cu, 140,000 oz. Ag. and 850 oz. Au; in cathodes 180,000 lb. Cu; in solutions 95,000 lb. Cu; or a total of 2,597,300 lb. Cu, 184,000 oz. Ag, and 1166 oz. Au.

It is generally held that a plant having a daily capacity of 100 tons of copper, casting anodes as well as cathodes, costs about \$450,000 excluding the precious metal that is tied up. The cost of refining by the multiple process at Anaconda in 1897-98 with a yearly output 30,000 tons of copper was 0.75

<sup>1</sup> Burns, *loc. cit.*

cents per pound or \$15 per ton of copper produced.<sup>1</sup> With increase of size of plant and improvement in the methods of handling and of operating, the cost in Eastern refineries with a daily capacity of 200 tons and over is from \$4 to \$5 per ton of copper, excluding all overhead charges. The old rule that 1 ton of coal is required for 1 ton of cathode copper still holds good to-day.

The curve given in Fig. 529, drawn by L. Addicks,<sup>2</sup> shows the relation that exists between the current density and the cost of power in the different plants of the United States using the multiple process.

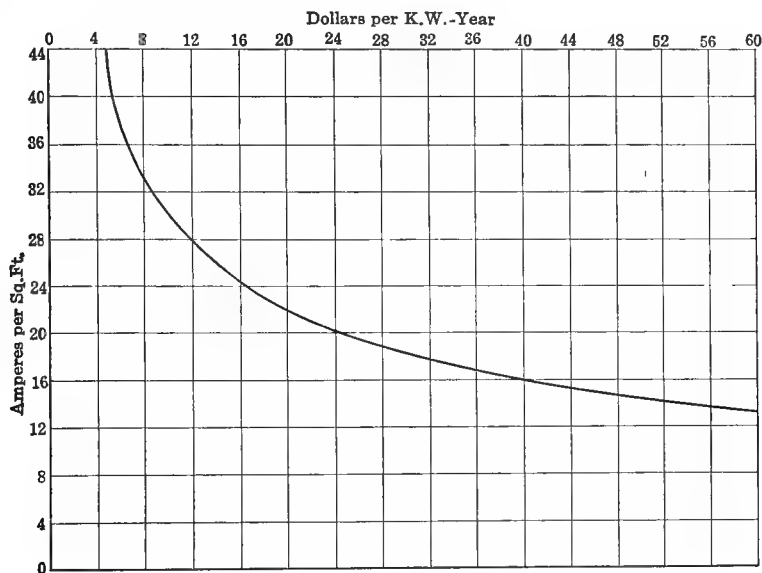


FIG. 529.—Current density vs. cost of power (Addicks).

**266. Examples of Multiple Process.**—Three examples may serve to show the general arrangements of multiple plants: Anaconda, erected in 1904; Great Falls, remodeled in 1896; and Raritan No. 2, erected in 1908.

(a) THE ANACONDA PLANT (Thofern System),<sup>3</sup> shown in Figs. 530-534, has 1400 tanks divided into 7 sets of 200 each. Each set, made up of 2 blocks of 100 tanks, receives from its generator a current of 4000 amperes at 60 volt to be distributed according to the Thofern system (Figs. 521-522).<sup>4</sup> The positive current, arriving between two blocks, traverses one block to the left of the North-South aisle in zig-zag as indicated, passes to the other block on the right of the aisle, supplies its tanks with electricity along similar paths as the first, and leaves

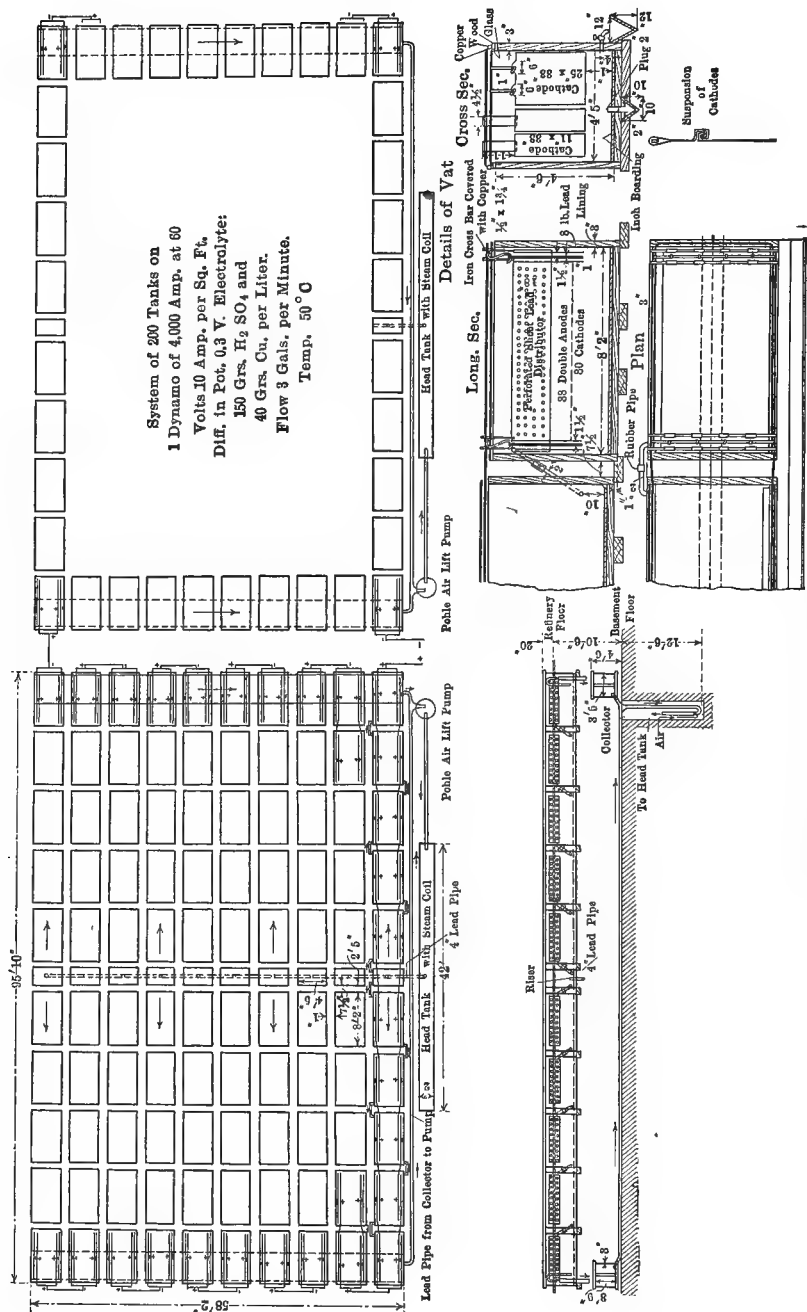
<sup>1</sup> Keller, *Min. Ind.*, 1898, VII, 236.

<sup>2</sup> See also *Met. Chem. Eng.*, 1914, xii, 91.

<sup>3</sup> Corresp., *Eng. Min. J.*, 1896, LXII, 271; Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 308; D. H., *Zt. Electrochem.*, 1901, VII, 793; not operated at present.

<sup>4</sup> Fontaine, *Eng. Min. J.*, 1892, LIII, 669.

Hering, *Berg. Hüttenm. Z.*, 1893, LII, 53.



FIGS. 530-534.—Anaconda electrolytic refinery.



the set opposite the place of entrance. The electrolyte, 40 g. Cu and 150 g.  $\text{H}_2\text{SO}_4$  per liter, brought to  $50^\circ\text{C}$ . in the head-tank of a block by a steam-coil, flows through a 4-in. pipe into 10 communicating distributing boxes. Each box feeds 10 electrolyzing vats arranged in two cascades on either side. The last vats of the cascades on both sides discharge into two collector boxes which, connected by a pipe, feed the Pohlé air-lift pump which raises the electrolyte to the head-tank. The circulation between the individual vats is effected by drawing off the electrolyte at the side of one tank, 10 in. above the bottom, through an inclined lead pipe, broken and connected with rubber hose to prevent any stray current from passing, and delivering it on the same side near the top of the next vat back of a distributor of perforated sheet lead. With a current density of 10 amperes per square foot cathode area, the circulation is only 3 gal. per minute. The individual vats, 8 ft. 2 in. by 4 ft. 5 in. and 4 ft. 6 in. deep, are of 3-in. planks lined with 8-lb. lead; the bottoms are covered with 1-in. boards. In the side of a vat is a cock, 4 in. above the floor, to draw off electrolyte, and in the bottom a 2-in. plug to close the opening for removing anode mud (Cu 10 per cent., Ag 18,000, and Au 100 oz. per ton), into a trough leading to a collecting tank, to be screened and forced by an acid-egg into the silver department. The furnace-refined converter anodes,  $32\frac{7}{8}$  in. long by  $24\frac{1}{4}$  in. wide by  $1\frac{1}{4}$  and 1 in. thick, weighing 230 lb. (Cu 99 per cent., Ag 90 and Au 0.5 oz. per ton) are suspended by two hooks in pairs from iron copper-coated cross-bars; they are corroded in 37 days and make 7 per cent. scrap. The starting cathodes, 33 by 11 in., weighing  $\frac{3}{4}$ -1 lb., are clamped to strips of copper and suspended in fours from a cross-bar; they are removed when their several weights have reached about 100 lb., or when the anodes have been completely corroded. An analysis shows Cu 99.96, As 0.0009, Sb 0.0023 per cent., Ag 0.25 oz. per ton. The fall in potential between vats is 0.3 volt. The 38 anodes or the 80 cathodes of a vat are put in place and removed together; the cathodes are taken out individually, two days after they have been placed, in order to be straightened.

(b) THE GREAT FALLS PLANT.<sup>1</sup>—This plant was erected in 1903 and has been in almost continuous operation since then. It has undergone several changes to meet the demands of the increased output of the smelting departments. In 1893 there were produced 3179 tons of copper; in 1912 the product was 31,596 tons, which meets the market requirements west of Chicago, Ill.; the greater part of the copper of the smeltery is refined at the works of the Raritan Copper Co., Perth Amboy, N. J., discussed below.

The flow-sheet of the refinery is given in Fig. 535, and plans and sectional elevations of the tank and sulphate buildings are represented in Figs. 536-541. The tank building contains 20 double rows (Figs. 519-520) of 16 tanks (Figs. 505-506), each with 22 converter anodes with 40 oz. Ag and 0.24 oz. Au per ton (Figs. 498-499) and 22 cathodes (Figs. 508-509). A double row of tanks forms a cascade (Figs. 519-520, and 541). At the head of the tank room is the pump room with three sumps for electrolyte and corresponding Pohlé air-

<sup>1</sup> Hofman, *Tr. A. I. M. E.*, 1904, XXXIV, 308.

Burns, *op. cit.*, 1913, XLVI.

TABLE 128.—THE MULTIPLE PROCESS IN THE

	Raritan Copper Co., Perth Amboy, N. J.	American Smelting and Refining Co., Maurer, N. J.
<i>Electrolyte:</i>		
Composition { per cent. Cu.....	3.5	3.1
per cent. free H <sub>2</sub> SO <sub>4</sub> .....	12.5	12.0
Temperature—deg. C.....	60	57
Circulation—gallons per minute.....	3.5	6.0-6.5
Circulation apparatus.....	Antisell pump	Antisell pump
<i>Current:</i>		
Ampères per square foot cathode.....	18	12-13
Voltage, fall in, per tank.....	0.30	0.30
Total current from 1 generator, amp. × volts.....	7000 × 128	6500 × 132    4100 × 125 7300 × 125    4150 × 125
<i>Anode:</i>		
Composition.....	Cu 99.3	Cu 97-98, Ag 1.0
Length, width, thickness (top and bottom).....	36 × 28 × 1½ t = b	36 × 32 × 1 t½" > b
Weight, pounds.....	500	450
Mode of suspension.....	Shoulder	Shoulder
Corrosion, exchanged after days.....	28	28
Per cent. scrap.....	12 15	14
<i>Cathode:</i>		
Starting sheet, length × width × thickness, inches.....	30 × 37 × ⅛	38 × 34 × ⅛
Weight, pounds.....	11	11-12
Mode of suspension.....	Morrow clip	Morrow clip
Exchanged, after days.....	7	14
Weight, pounds.....	125	185
<i>Manipulation of electrodes</i> .....	Overhead electric crane	Overhead electric crane
<i>Deposition vat:</i>		
Length × width × depth.....	12' × 3' 4" × 3' 6"	11' × 3' 6" × 3' 6"
No. anodes, cathodes.....	26, 27	28, 29
Electric connection.....	Walker	Walker
Busbar, cross-section.....	9 × 1½	20 sq. in.
Amp. per sq. in. cross-section.....	620	540
<i>Anode mud:</i>		
Per cent. of anode.....	0.6	1.8
Composition, per cent.....	Ag-60 Cu-20	.....
Removed, after days.....	28	14
Referred to on pages: .....		

## ELECTROLYTIC REFINERIES OF THE UNITED STATES

U. S. Metals Refining Co., Chrome, N. J.	Balbach Smelting and Refining Co., Newark, N. J.	Calumet & Hecla Mining Co., Buffalo, N. Y.	Boston & Montana Consolidated Copper and Silver Mining Co., Great Falls, Mont.	Anaconda Copper Mining Co., Anaconda, Mont.
3.0 12.0	4.0 10.0	4.5 13.8	3.3 13.0	4.0 15.0
54	50-57	49-40.5	64	50
3.5	4	3	5	3
Antisell pump	.....	Pohlé air-lift pump	Pohlé air-lift pump	Pohlé air-lift pump
20	20	11	34	10
0.38	0.3	0.22	0.6	0.3
10,500×100	5000×75	2000-2200×250	4500×180	4000×60
Cu 99.25	Cu 98-99 variable Ag Au(As+Sb)>.2 Ni, etc.	.....	Cu 99.1 Ag 0.13	Cu 99.25 Ag 0.3
36×36×t=b	36×24×1½ t½">b	28.5×24×1.8 28×30×1.5 t=b	35×24 3" t 2½" b	32½×24½ 1½" t 1" b
475	350	400	500	230
Shoulder	Cast lugs	Lugs with hooks	Morrow clip	Lug
20	24±	60	18	37
15	15-20	8	8	7
40½×38½×0.114	37×25(×⅙?)	29½×25 29×31	36½×26	33×11
8-10	7	6 and 7	2½	½-1
Loop	Loops	Straps	Morrow clip	Clamped loop
10	10	30+	■	37
.....	140	170	55	100
Overhead elec- tric crane	Overhead trolleys 2 hand hoists	Cranes	Overhead crane	Overhead elec- tric crane
11'×3'6½"× 3'7½"	9'×28"×44"	9' 1½"×33½"×32" 9' 1½"×33½"×38"	9' 9"×2' 4"×3' 9"	8'2"×4'5"×4'6"
30, 31	21, 22	20, 21	21, 22	38, 80
Walker	.....	Cross bars	Double rows	Thofner system
20 sq. in.	.....	Mains 2½"×1½" On tanks 2"×1"	4½ and 3½"×1½"	.....
500	700-900	.....	.....	.....
1.25	1	0.20	.....	.....
Ag 34 Cu 15	Ag+Au 25-40 Cu 15-20 Rest As, Sb, Pb, etc.	Cu-35 Sn-1 As-3 Ag-55 Small amounts of Pb-6 Se, Te, Sb, Ni, Co	Cu 43 Ag 17	Cu 10 Ag 62
10	30	60	60	.....

lift pumps and distributing tanks. Next to the pump room are one set of starting-sheet tanks of the same dimensions as the depositing tanks, each with 22 anodes and 21 cathode-blanks of  $\frac{1}{4}$ -in. sheet copper 27.5 by 39.5 in.; four purifying tanks; and two reducing tanks. The crane room contains a 7-ton crane for handling cathodes and scrap. Anodes and cathodes are handled four at a time with a 1-ton Yale & Towne triplet chain block and multiple hook; they arrive and are deposited in buggies, and are weighed in the crane and scale room.

The electrolyte (analysis, Table 129) contains per liter 40 g. Cu and 160 g.  $\text{H}_2\text{SO}_4$ , and is circulated at the rate of 6 gal. per minute. The current density is

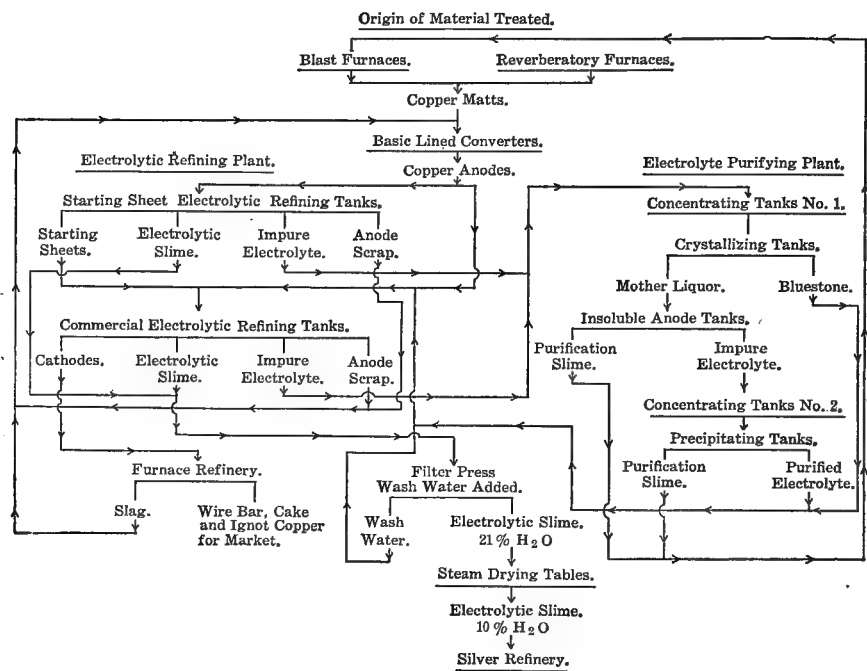
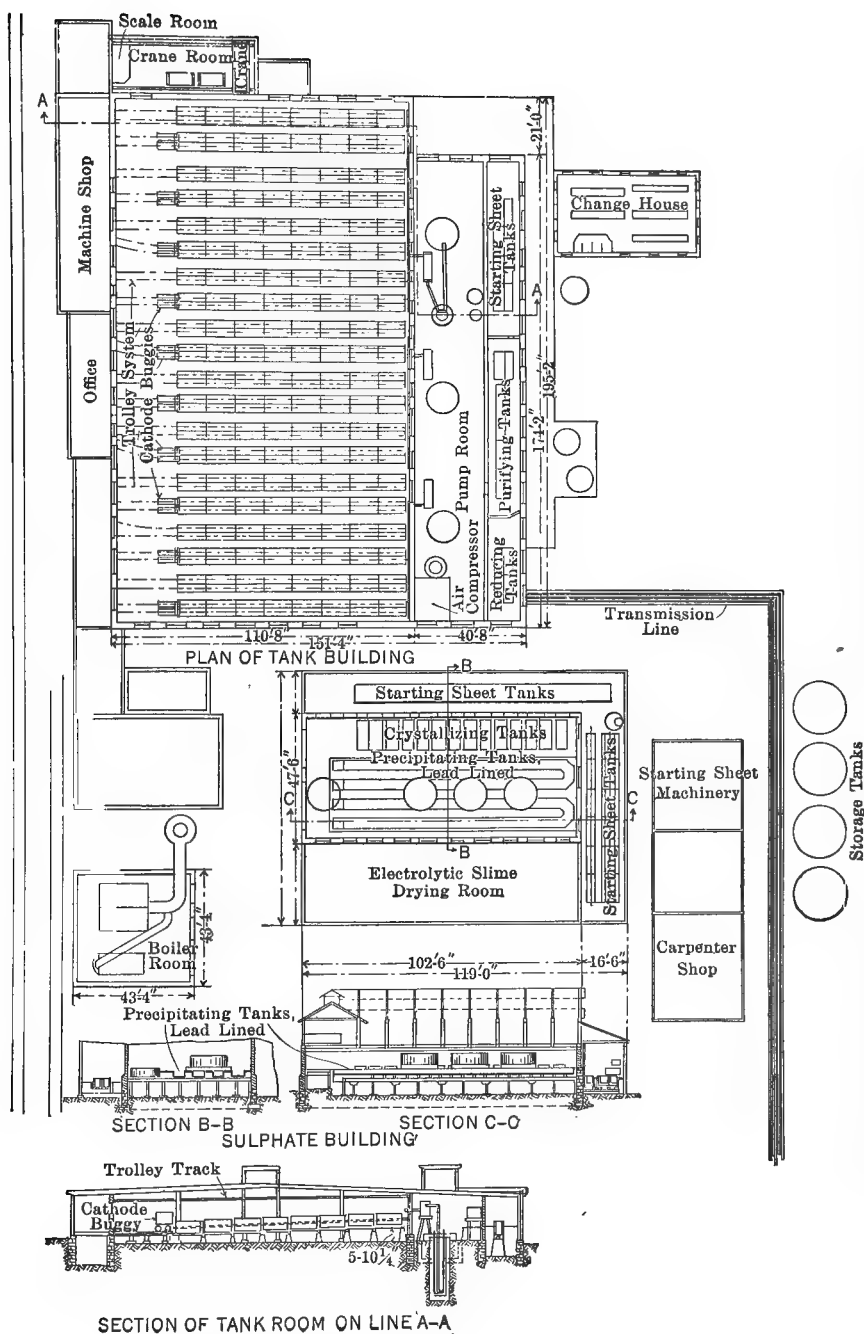


FIG. 535.—Flow-sheet of Great Falls electrolytic refinery.

34 amp. per square foot cathode area. Cathodes are removed every 2 days. An anode of 500 lb. weighs 30 lb., when returned to the converter. The anode mud is taken out once in 60 days when about 5.5 in. will have collected. A copper jumper, Fig. 521, serves to disconnect the tanks that are to be cleaned; a bronze steam-injector to transfer the mud over  $\frac{1}{2}$ - and  $\frac{1}{8}$ -in. screens into a lead-lined tank, 12 ft. in diameter and 4 ft. deep, where it is washed with water, drawn off into a cast-copper lead-lined *montejus*, and forced through a Bushnell filter-press, containing hard-copper plates and 8-oz. duck filters. This furnishes 13 cakes, 26 in. in diameter and 1.25 in. thick, which retain 20 per cent.  $\text{H}_2\text{O}$ . The cakes are dried on copper steam-drying tables, Fig. 538,



FIGS. 536-541.—Plans and sectional elevations of tank and sulphate buildings, Great Falls electrolytic refinery.

until half of the water has been expelled; crushed with a roller on a cement floor; and sampled in 22,000-lb. lots for shipment.

The sulphate building, Figs. 538-540, with the additional starting-sheet tanks and the machinery for preparing the sheets, contains three boiling tanks for concentrating electrolyte, the necessary crystallizing vats for blue vitriol, and precipitating tanks for treating mother liquor freed from part of its copper in the form of blue vitriol.

The current is furnished by two Westinghouse, shunt-wound, engine-type, 810-kw. generators having a normal capacity of 4500 amp. at 180 volt with a speed of 130 r.p.m. The average output of the machines is 4600 amp. each at 222 volt or 1021 kw., equivalent to 26 per cent. overload. The generators are driven by water-power. The current is conducted to the tank building through slabs of cast copper joined by overlapping ends fastened with iron bolts; expansion joints in the form of cast-copper arches take care of changes of temperature.

(c) THE RARITAN PLANT, NO. 2 (WALKER SYSTEM).—The plan of the tank house is given in Fig. 542. The building, 582 ft. long by 149 ft. 6 in. wide, has in the tank room on the main floor three parallel rows of tanks, each of which is served by two 10-ton three-motor overhead cranes, 19 ft. 8 in. above the floor, for handling anodes and cathodes. Beneath the main floor, supported by concrete pillars (Fig. 512), is a light cellar 9 ft. 9 in. high with acid-proof floor consisting of 6 in. concrete covered with pitch and overlain by a 2-in. course of chemical brick with pitch joints. The floor drains through gutters to a sump. The building is warmed with exhaust steam and has artificial ventilation to keep everything dry and thus prevent leakage of current. The air is changed by a rotary fan once in 20 min.; 75 per cent. of the air goes through the cellar, 25 per cent. through the room. There are 1188 tanks in the room grouped in three rows of 396 tanks; a row has 36 nests, and a nest 11 tanks, 10 ft. long by 2 ft. 8 in. wide by 3 ft. 11 in. deep. There is one liberating tank for every 44 electrolyzing tanks. The engine room has four generators, one of which is held in reserve; a generator requiring 1250 h.p. furnishes 396 tanks with a current of 7500 amp. at 145 volt. The heavily-dotted lines show the passage of the current from the generators to each of the three rows of tanks, through which it travels lengthwise. The current density is 20 amp. per square foot cathode area. The main conductors have a cross-sectional area of 12.75 sq. in. and receive a current of 500 amp. per square inch. The fall in potential from anode to cathode is 0.210 volt, and from tank to tank 0.360 volt. At the ends of the building, opposite the stripping benches, are the vats for preparing the starting sheets; nearby are shears and Moore looping machines. In the cross-aisles are washing boxes to clean corroded anodes before they are returned to the anode furnace, and to dip cathodes twice in hot water to wash off adhering electrolyte; in the same aisles are stands or racks for a complement of anodes and cathodes to be taken to or from the vats. In the pump room are six Antisell centrifugal pumps (Figs. 495-496). The return electrolyte flows into six sheet-iron lead-lined pump boxes of 4 cu. ft. capacity which overflow either into three emer-

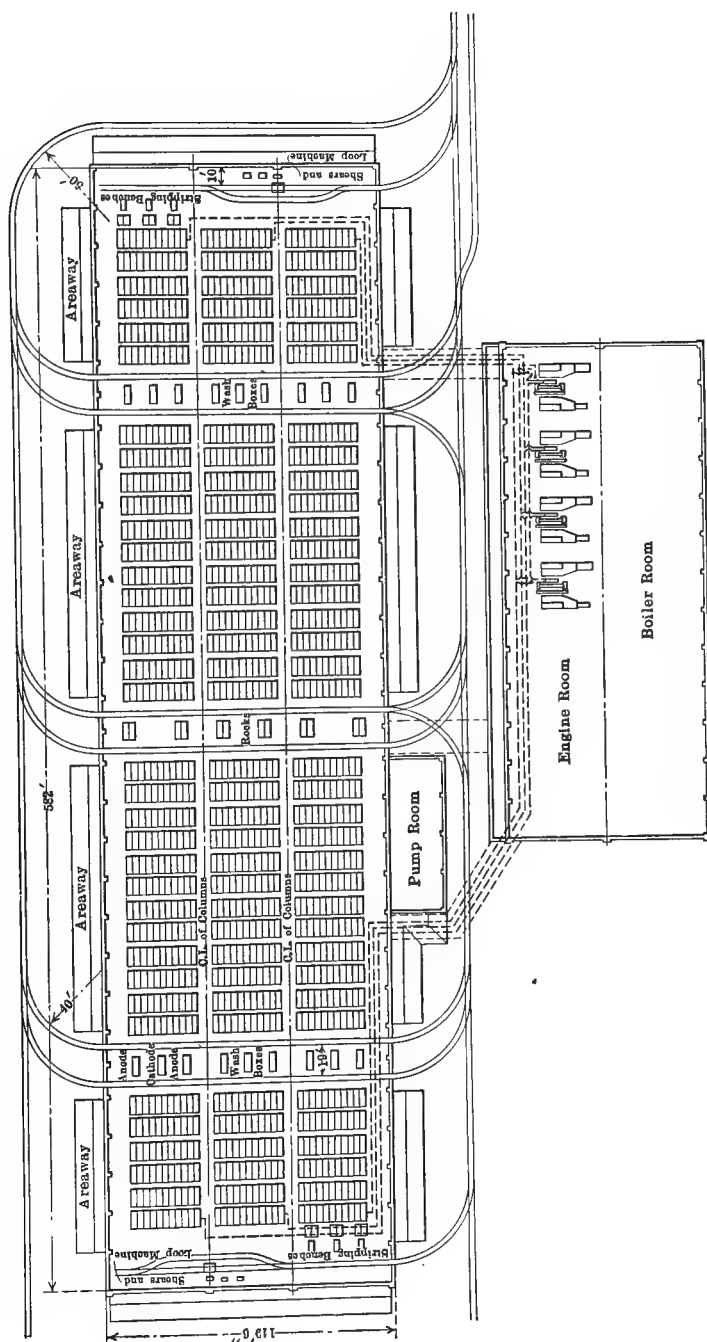


FIG. 542.—Plan of tank house No. 2 Raritan Copper Co.

gency tanks, 16 ft. in diameter and 12 ft. deep of sheet iron and lead-lined, or normally into the inlet pipes of the pumps. The electrolyte is raised 27 ft. and delivered to one of the 6 heating tanks, 28 by 4 ft. and 4 ft. deep, provided with 12 lead steam pipes, 1.5 in. diameter, to raise the temperature to about 50° C. For the circulation of the electrolyte, containing 3 per cent. Cu and 12 per cent. free  $\text{H}_2\text{SO}_4$ , the tank room is divided cross-wise into six units, two at the ends, and four in the center, each with 198 tanks. A unit with its six cross-rows of tanks is served from a centrifugal pump; two neighboring cascades are fed from one branch pipe. The rate of circulation is 4 gal. per minute, and the system is shown in Fig. 491. The construction of the tanks has been given in Figs. 511-515; a tank contains 24 anodes, 36 by 28 by 2 in., and 25 cathodes, 37 by 30 in., giving it an active cathode surface of 369.5 sq. ft. An anode weighs 475 lb., and has shoulders 1 in. thick narrowed toward the ends so that the center of gravity lies near them. A starting cathode is ready after 42 hr. deposition. An anode remains in the vat for 28 days and furnishes from 12 to 13 per cent. scrap of which 5 per cent. is in the shoulders; a cathode remains 14 days and weighs 160 lb. A tank is cleaned up, when the anodes are exchanged. The working-up of the mud has been discussed in § 262.

There are locked up in the plant, in rods, plates, busbars, leads, etc., 581,000 lb. Cu, in the electrodes under treatment 10,000,000-11,000,000 lb., and in the electrolyte 240,000 lb. The lead used in construction, pipes, anodes, etc., totals 1,370,000 lb.

(d) TABULATED DATA.—Table 128 contains the leading facts of the principal electrolytic plants of the United States using the multiple process.

The refineries of Lithgow<sup>1</sup> and Port Kembla<sup>2</sup> have been described in the accompanying references.

## B. SERIES SYSTEM

**267. Series (Hayden) System in General.**—In this process cast or rolled electrodes of high-grade copper are placed vertically in series in an electrolyzing vat charged with acidulated blue vitriol so as to fit closely the sides. Fig. 543 gives a diagrammatic sketch. As the current passes through the vat, the electrodes, with exception of those at the ends, become negatively charged on the sides facing the entrance and positively on the sides facing the exit of the current. The positive current entering through one end electrode, which

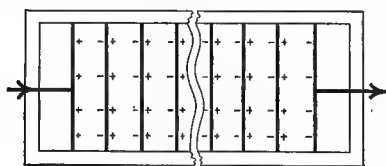


FIG. 543.—The series (Hayden) system.

is solely anode, causes Cu to be dissolved and to be deposited on the negative side of the next following intermediary electrode, while on the positive side of the latter Cu goes into solution, and so on through the vat to the last

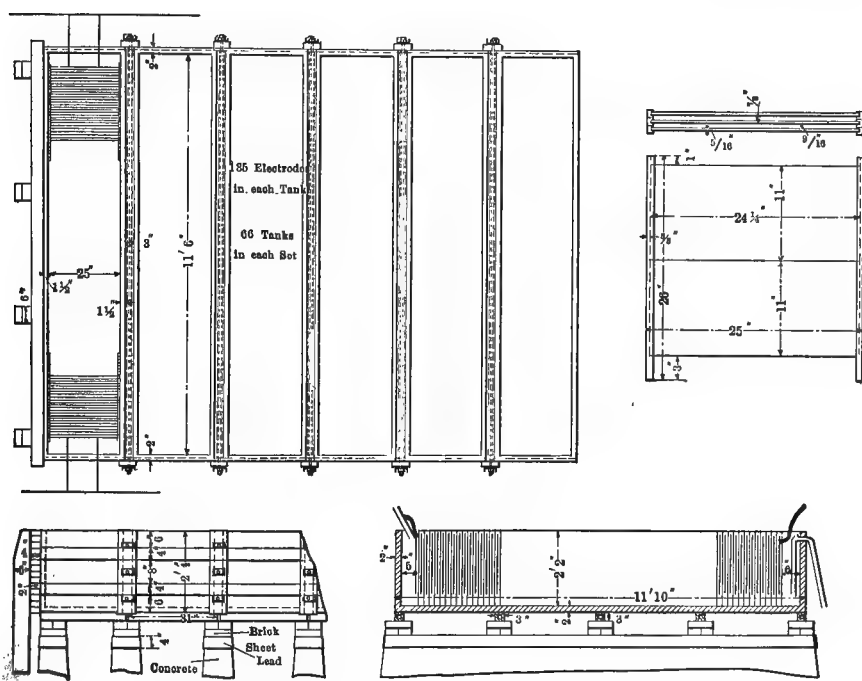
<sup>1</sup> *Eng. Min. J.*, 1910, XC, 717.

<sup>2</sup> *Met. Chem. Eng.*, 1912, X, 694.



electrode which, solely cathode, is connected with the exit wire. In this manner the copper is dissolved and deposited until the original intermediary electrodes, anodes on one side and cathodes on the other, have been changed into electrodeposited copper, and the end electrodes have become lighter or heavier. The insoluble impurities and precious metals collect on the bottom of a vat as anode mud. The pure copper and the anode mud are worked up as in the multiple process.

The Hayden process<sup>1</sup> has outlived the other two series processes of Smith and of Randolph. In the former, the electrodes were placed horizontally and



FIGS. 544-548.—Tank-details of the Baltimore electrolytic refinery.

separated by diaphragms, and the current entered at the top; in the latter it entered at the bottom. Stalman's idea<sup>2</sup> of riveting sheets of copper to the negative sides of the vertical intermediary electrodes of Hayden, and thus facilitating the removal of the last of any undissolved electrode from the newly deposited copper, has been found to be unnecessary. In the Hayden process, then, the vertical electrodes of a vat are connected in series, and the vats in multiple. Series processes are in operation in the United States at the works of the Nichols Copper Co., Brooklyn, N. Y., and the Baltimore Copper Smelting & Rolling Co., Baltimore, Md.

<sup>1</sup> Badt, *Eng. Min. J.*, 1892, LIV, 126.

<sup>2</sup> U. S. Patent, No. 467350, 467484, January 18, 1892.

**268. The Baltimore Plant.**—As little information is available regarding the Nichols refinery,<sup>1</sup> the present discussion is confined to the Baltimore plant, of which tank details are given in Figs. 544-548.

**269. Electrolyte.**—The composition, temperature, and circulation of the electrolyte are about the same as in the multiple process. It contains 12 per cent. blue vitriol and 9 per cent. free  $\text{H}_2\text{SO}_4$ ; the circulation is 2.5 gal. per minute; the temperature 40-43° C. The electrolyte is siphoned from the bottom of the vat at the discharge end instead of being made to overflow. The siphon is shown in Fig. 546; it has an orifice at the top which serves as an overflow and starts the siphon, whereupon the regular flow begins near the bottom of the tank.

**270. Current.**—The current connection is made through conductor bars at the ends of a tank, Figs. 544-546. The current density is 21 amp. per square foot and the electromotive force 22 volt with a vat holding 135 electrodes; the fall in potential from plate to plate is about  $\frac{1}{6}$  volt. On account of the high voltage there is a strong leakage of current, which reduces the ampere efficiency to from 65 to 67 per cent.

**271. Electrodes.**—The electrodes are rolled sheet copper. In order to permit rolling, the copper must be of good quality and may not contain too much  $\text{Cu}_2\text{O}$ ; hence blister copper from the reverberatory furnace or the converter has to undergo a partial fire-refining before it may be cast into suitable cakes. A small addition of Pb, not over 0.1 per cent., to the refining charge improves the rolling quality of the copper.

TABLE 129.—COPPER SUITED AND UNSUITED FOR ROLLING ELECTRODES<sup>2</sup>

Copper	Pb	Bi	Sb	As	Se and Te	Ag, oz. per ton	Au, oz. per ton
Suited for rolling.....	0.0082	0.0025	0.0443	0.0068	0.0071	.....	.....
Suited for rolling.....	0.0093	0.0320	0.0651	0.0586	0.0098	.....	.....
Unsuited for rolling.....	0.0558	0.0274	0.1245	0.1160	0.0153	100.60	0.45,
Unsuited for rolling.....	0.0073	0.0340	0.1350	0.0582	0.1067	229.40	0.12
Suited for rolling after adding Pb.	0.0069	0.0095	0.0602	0.0312	0.0527	156.30	0.48
Suited for rolling after adding Pb.	trace	0.0055	0.0370	0.0255	0.0365	172.90	0.60

Toughened copper from a 250-ton reverberatory furnace is run into ladles, of 6000 lb. capacity, placed on trucks; they discharge their contents into a retaining tilting-ladle of 20,000 lb. capacity, from which billets weighing 490 lb. are cast at the rate of 60 tons per hour by means of a rotating-table casting machine with 40 molds  $10\frac{1}{2}$  by 42 by  $3\frac{1}{2}$  in. The red-hot billets are dropped onto a conveyor which delivers them to the first of a series of 5 two-high continuous rolls, 21 in. in diameter, which roll the billets into sheets  $\frac{5}{16}$  in. thick at the rate of 10 tons per hour.<sup>3</sup> From the fifth roll, the sheet is transferred to

<sup>1</sup> Cast electrodes 10 by 59 by  $\frac{3}{8}$  in., weighing 67 lb.; wooden vats lined with pitch; electrolyte kept cool to prevent flowing of pitch.

<sup>2</sup> Keller, *Min. Ind.*, 1898, VIII, 233.

<sup>3</sup> Editor: "Rolling Copper," *Iron Age*, 1907, LXXX, 507.

a sixth roll, in line with the fifth but moving in the opposite direction, which delivers the sheet into a water-trough provided with rollers. The cooled sheet goes to crocodile shears which cut it into electrodes 11 by  $24\frac{1}{4}$  by  $\frac{5}{16}$  in., forming 6 per cent. scrap from the ends. The electrodes are straightened under a drop-hammer and go to the frame division, Figs. 547-548, where two are placed by hand between a pair of grooved wooden strips; the joints on the positive sides are then painted with tar to facilitate the removal of the deposited copper from any remaining electrode material. The difference between the commercial cathode and the cathode freed from all electrode scrap is shown in Table 130.<sup>1</sup> Series-copper usually contains 1.5-2.0 oz. Ag per ton; multiple-copper 0.3 oz.

TABLE 130.—CATHODE FROM THE HAYDEN SYSTEM

Cathode	Pb	Bi	Sb	As	Ag. oz. per ton
Commercial.....	0.00047	0.00018	0.00136	0.00059	1.11
Freed from all scrap.....	0.00055	.....	0.00094	0.00025	0.36

**272. Depositing Vat.**—On account of the high voltage in the series process and the consequent danger of shortcircuiting, the usual construction of the vats of wood lined with lead is impracticable. Formerly the vats were of slate with joints made tight by a tar cement; the sides were coated with tar, and the tops covered with slats. At present, Figs. 544-546, the tanks, 11 ft. 6 in. long by 25 in. wide by 26 in. deep, are composed of a mixture of asphalt, asbestos, and sand molded in place; 66 vats form a block, which rests on square glazed drain-tile pipes each carried by two courses of brick and concrete walls; between brick and wall is placed sheet lead to deflect any leakage of electrolyte. Between the several tanks are spaces 3 in. wide through which pass tie-rods, enclosed in lead pipe, connecting wooden buck-stays and channel-iron washers, which take up the end-thrust of the tanks through plates let into the tanks. The side-thrust of a block is taken up by a 4-in. wall built of 2-in. strips, the wall being held in place by posts buried in the ground. The spaces between the single tanks are filled with broken stone, and the interstices closed by pouring in molten sulphur. The 66 tanks of a block are connected in parallel and receive a current of 500 amp. at 220 volt.

**273. Corrosion and Deposition.**—Both proceed uniformly, and an electrode is corroded in 17 days. On the edge of the deposited copper there is usually found a small strip of electrode material, which is pulled off with nippers. At the center there remains sometimes a skeleton-like undecomposed patch of electrode which has to be removed.

**274. Clean Up.**—When the electrodes in a vat have been decomposed they are disconnected; the electrolyte is siphoned off; the cathodes are washed with a hose, being turned over like leaves in a book, removed, and the strips taken off; the copper is then transferred to the reverberatory furnace. The mud is sluiced out and worked up, as well as the fouled electrolyte, as in the multiple process.

<sup>1</sup> Keller, *Min. Ind.*, 1898, VII, 241.

## C. MULTIPLE VERSUS SERIES SYSTEM

**275. Multiple and Series Systems Compared.**<sup>1</sup>—The advantages claimed for the multiple system are: (1) Treatment of anode copper rich in precious metals and high in impurities; (2) handling of material in large units at low cost; (3) permissible variation in composition of electrolyte.

The advantages claimed for the series system are: (1) Smallness of power required per unit of deposited copper; (2) small amount of copper and precious metal locked up; (3) low percentage of scrap produced. (4) little space required per unit of copper deposited.

(1) IN THE MULTIPLE SYSTEM anodes with over 1 per cent. impurity and 400–1000 oz. AgAu per ton are frequently treated. In the series process the rolling of electrodes requires pure electrode material; the small electrode-distance, favoring the settlement of slime on the deposited copper, and the adhesion of anode material would cause the market copper to be rich in precious metal. In the series system therefore the electrodes should not contain over 0.166 per cent. impurity and not over 100 oz. AgAu per ton; 70 oz. is preferred.

(2) In the multiple system the electrodes and anode scrap are handled mechanically in large units, but in the series system the manipulation of electrodes and cathode copper is entirely by hand.

(3) In the multiple system there are open spaces between the vat and the electrodes, and the electrode distance is large, both of which permit a rapid circulation without danger of stirring up anode mud. The more rapid the circulation, the more impure can be the electrolyte without endangering the cathode copper, and the less frequent has to be its renewal.

(1) IN THE SERIES SYSTEM, as the electrode distance is small, the fall in potential is low; it is about one-half that of the multiple system, or 0.15 vs. 0.30 volt. This means that in the series system half the power will be required to deposit a given amount of copper as in the multiple. This advantage is offset by the great cost of casting thin electrodes or of rolling cakes into sheets when compared with the casting and handling in the multiple system.

(2) In the series system part of the copper in the busbars and all in the cross-bars is saved. The amount of copper and precious metal locked up in tanks is equal to the daily product multiplied by the time interval of the clean-up periods; i.e., in the series system the factor is 15, in the multiple it is 26 for copper and 33 for precious metal, allowing for scrap in both cases. With average copper bullion the interest on the metal locked up in the series system is one-half that in the multiple.

(3) The scrap produced in the series system amounts to 3 to 6 per cent. of the weight of the electrode; in the multiple the usual figure is 10 per cent. and often 13 per cent.

<sup>1</sup> Peters, "Modern Copper Smelting," 1895, p. 577.

Keller, *Min. Ind.*, 1898, VII, 229.

Haber, *Zt. Electrochem.*, 1903, IX, 384.

Editor, *Electrochem. Met. Ind.*, 1908, VI, 223.

Walker, *Min. Ind.*, 1908, XVII, 327.

(4) The series system formerly required much less floor space than the multiple. This does not hold good any longer, since refiners using the multiple system have increased the depth of the immersed anode; thus the U. S. Metals Refining Co. has anodes 3 by 3 ft., and requires 330 sq. ft. of tank room per ton of copper produced per day, a figure which is lower than in the series system.

SUMMARY.—The cost of operating by the two systems is about the same; the multiple has the advantage of being able to treat almost all classes of copper bullion, and of requiring less care in conducting tank room operations

Of the nine electrolytic refineries in the United States (Table 115), two have the series system, the rest the multiple.



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